Visualizing Catalysts in Action

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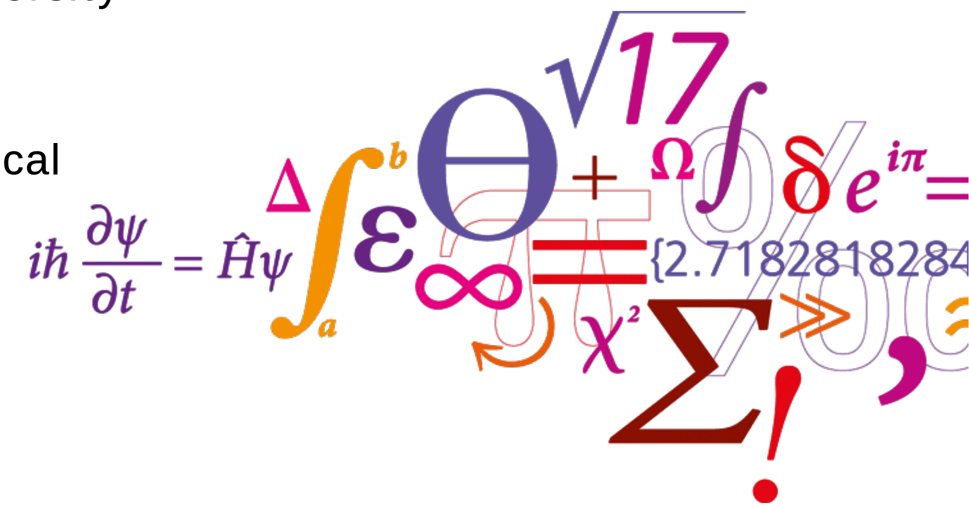

DTU Physics
Department of Physics

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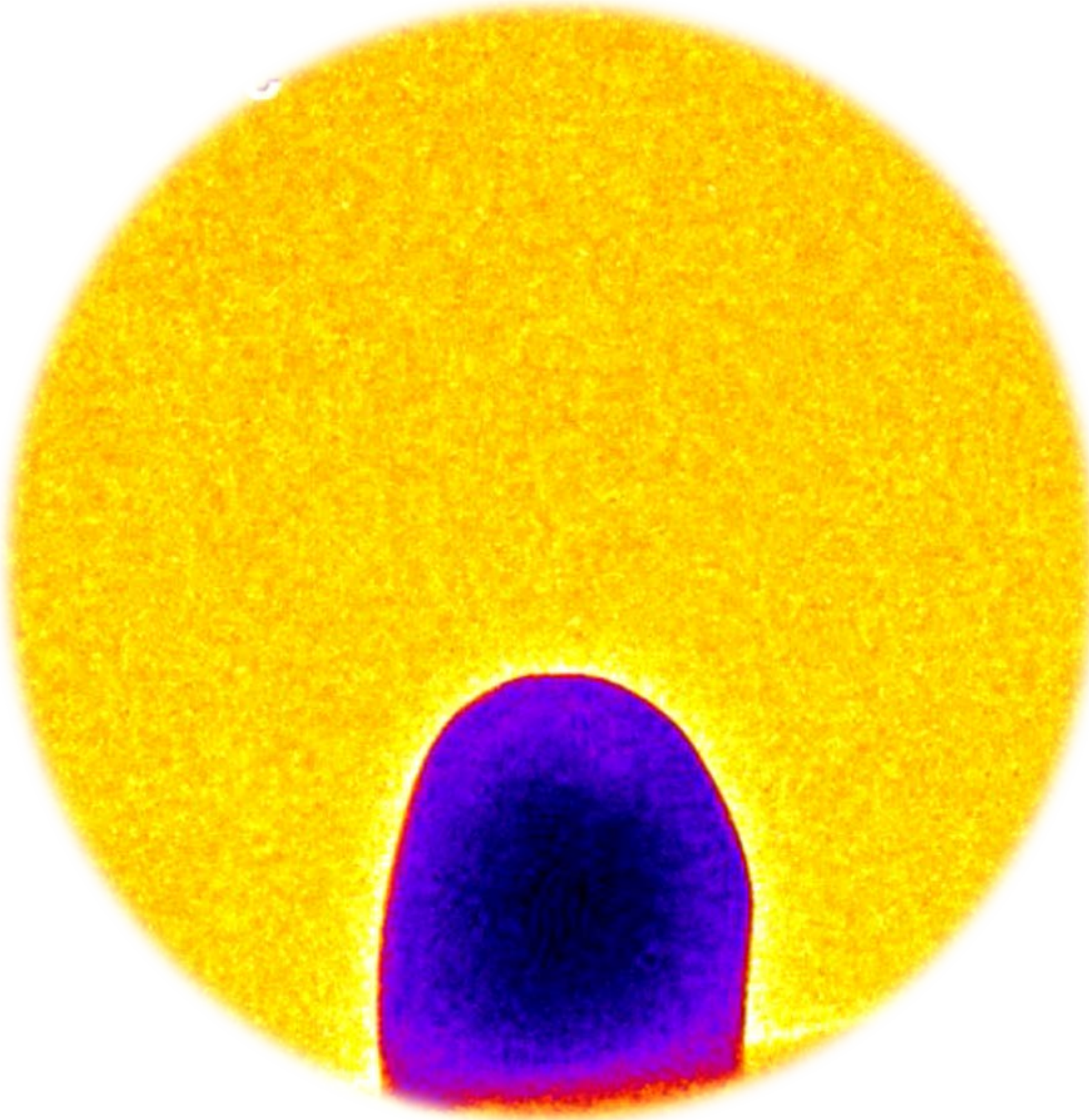
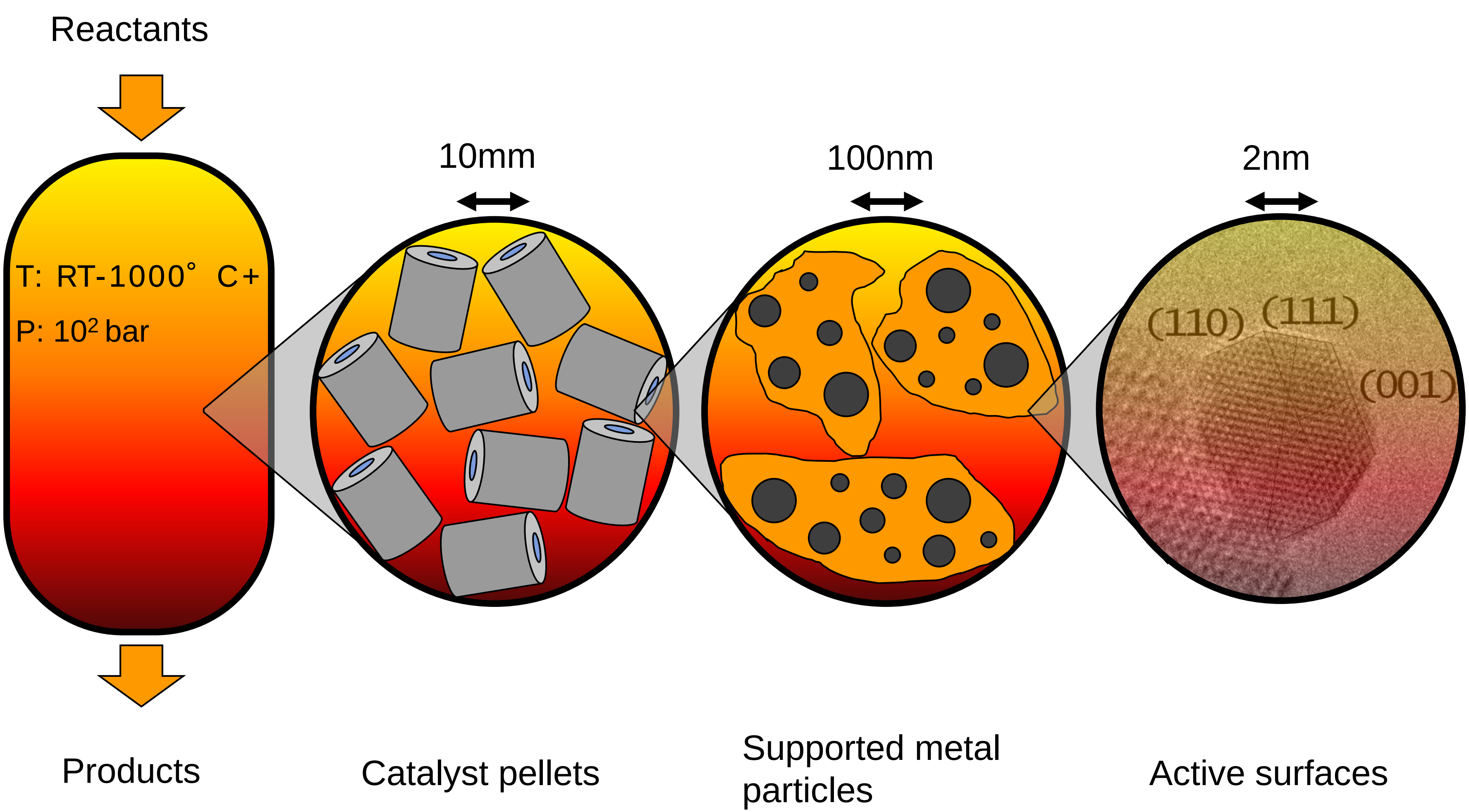
Thanks to the organizers



A Look Inside the Reactor



J.-D. Grunwaldt, J. B. Wagner, R. E. Dunin-Borkowski, ChemCatChem, 5, 65 (2013)

The in situ toolbox

			
Reactor	*In situ* XRD	*In situ* XAS	ETEM
			

Data acquisition and analysis				
Size	No		No	Yes
Morphology				Yes
Phase	No	Yes		
Activity	Yes			
Selectivity	Yes	(Yes)	(Yes)	No
Pressure	10^5-10^7 Pa	10^{-1}-10^5 Pa	10^{-1}-10^5 Pa	10^{-4}-10^3 Pa

Is it active?

What's the structure?

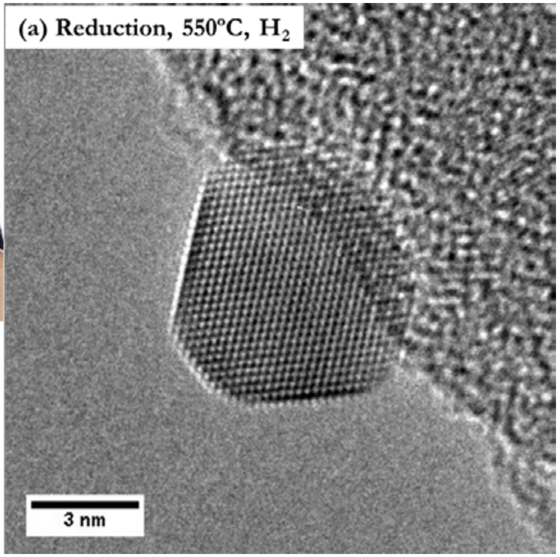
Can we optimize the synthesis?

What's the chemical state?

What's going on on the nano-scale

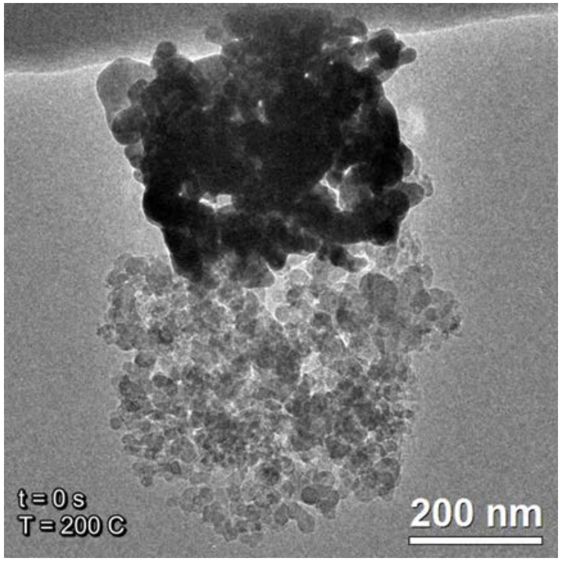
Complimentary information can be retrieved, BUT the sample state is DEPENDENT on the experimental limitations of the instruments

Dr. Elisabetta Fiordaliso



Outline

- The *in situ* toolbox
  - Environmental TEM
- The catalysts life cycle - Identical location and ETEM
  - Intermetallic $GaPd_2/SiO_2$ nanoparticles for low pressure CO_2 hydrogenation to methanol
- Watching the reaction - ETEM
  - Soot oxidation by Ag
- Summary and acknowledgement



Dr. Diego Gardini

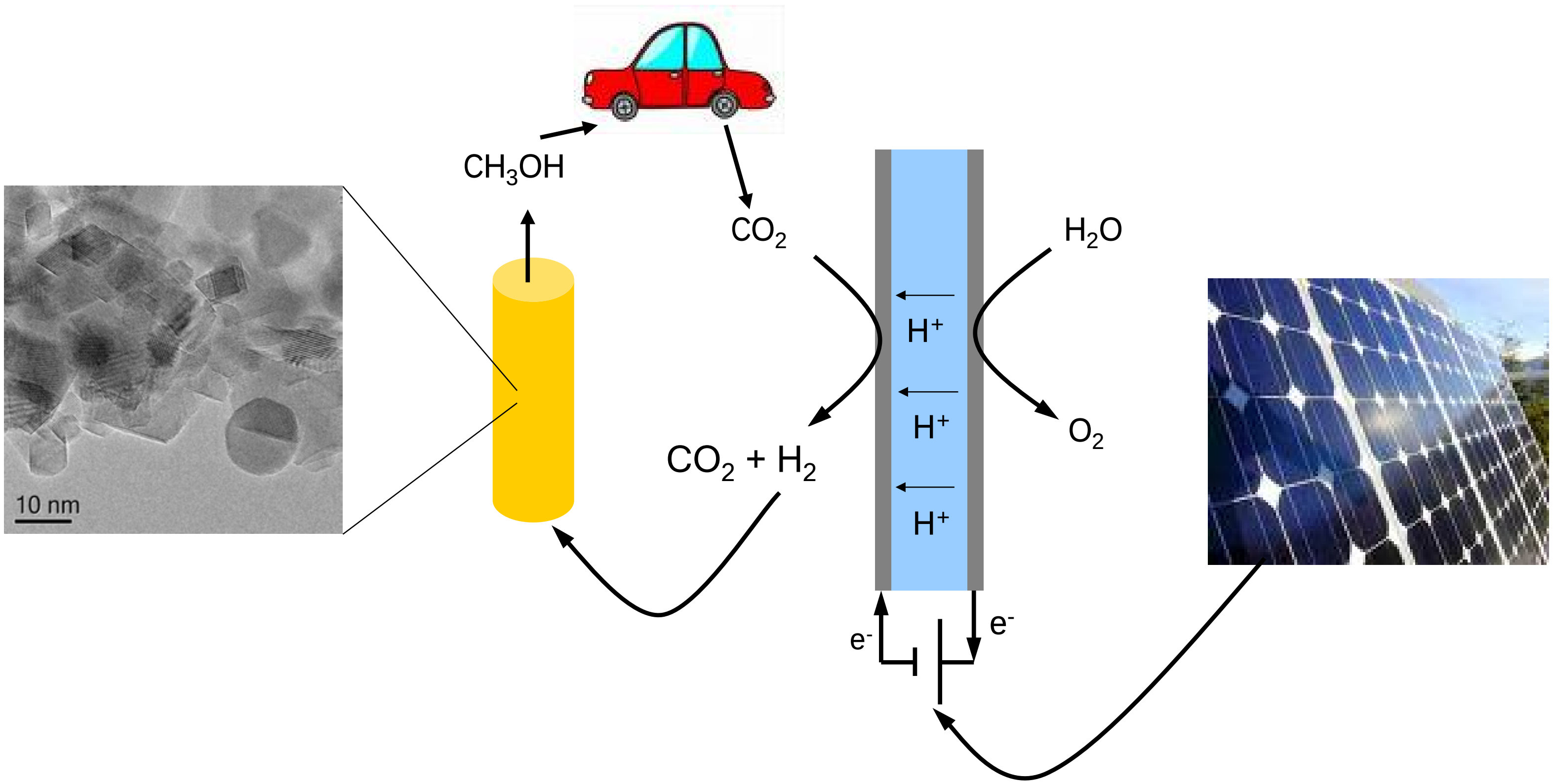
Dr. Elisabetta Fiordaliso

The catalysts life cycle - Identical location and ETEM

Intermetallic $GaPd_2/SiO_2$ nanoparticles for low pressure CO_2 hydrogenation to methanol

Methanol synthesis at lower temperature and pressure from CO_2

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$



Search for new catalysts

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

Requirements:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

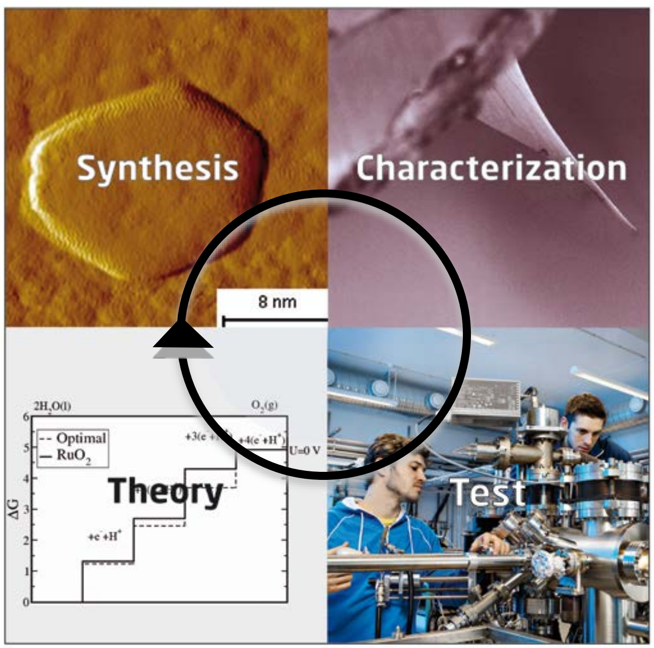
- Active at low pressure (1 bar)
- As selective as $Cu/ZnO/Al_2O_3$ (100%)
- Stable, resistant towards sintering and deactivation

Search for new catalysts

Candidates from DFT calculations:

Novel intermetallics Ni-Ga

F. Studt et al., “Discovery of a Ni-Ga Catalyst For Carbon Dioxide Reduction To Methanol”. Nature Chemistry 6.4 (2014): 320-324.



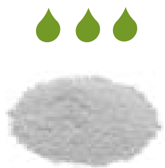
Pd_2Ga / SiO_2

T. Fujitani et al., “DEVELOPMENT OF AN ACTIVE GA2O3 SUPPORTED PALLADIUM CATALYST FOR THE SYNTHESIS OF METHANOL FROM CARBON-DIOXIDE AND HYDROGEN”. APPLIED CATALYSIS A-GENERAL 125.2 (1995): L199-L202.

1. Catalytic test

Sample preparation

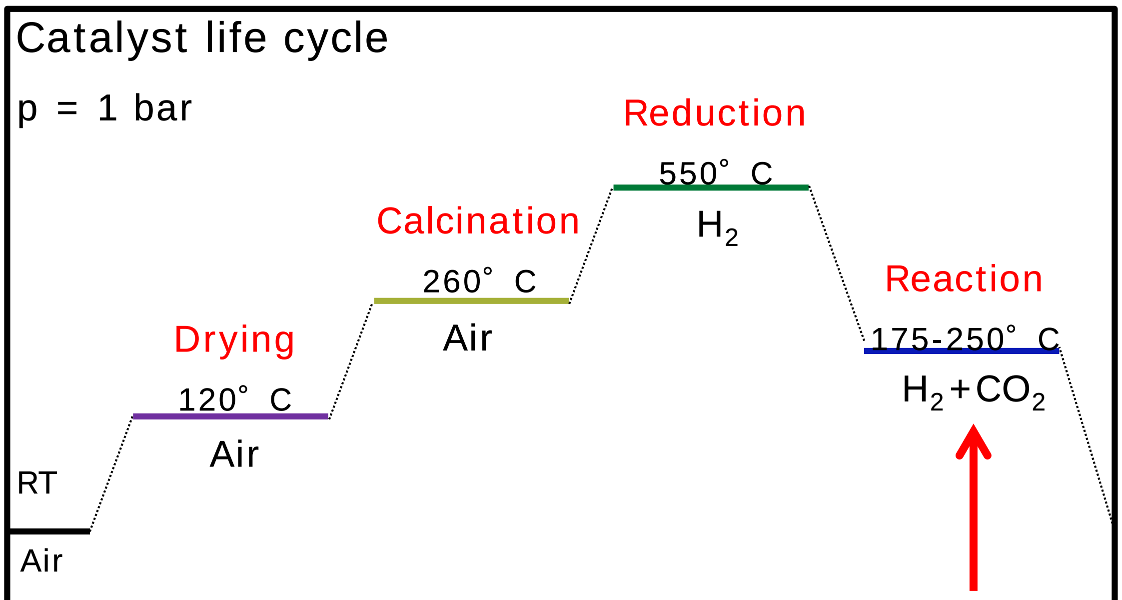
$Pd(NO_3)_2 + Ga(NO_3)_3 + HNO_3 + H_2O$



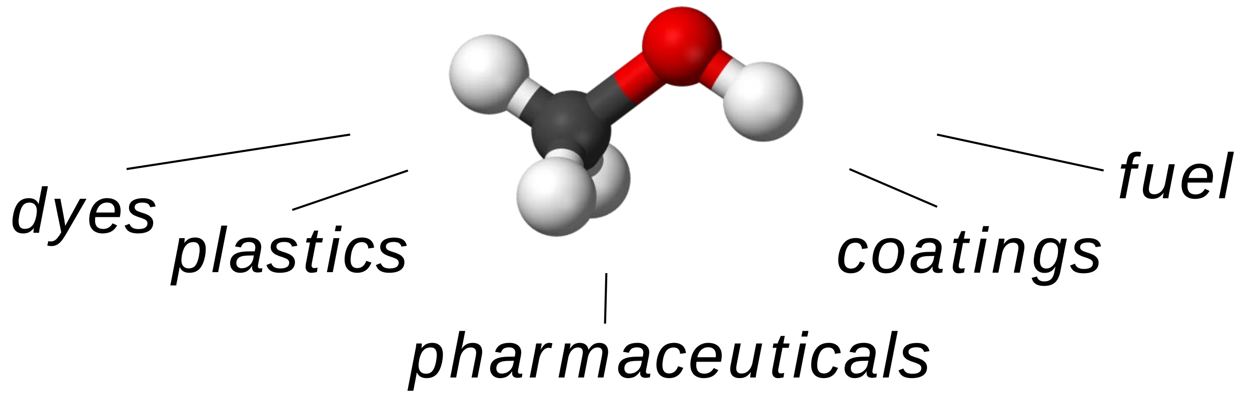
HSA SiO_2

Pd_2Ga / SiO_2

(23% metal loading)



Methanol synthesis



$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

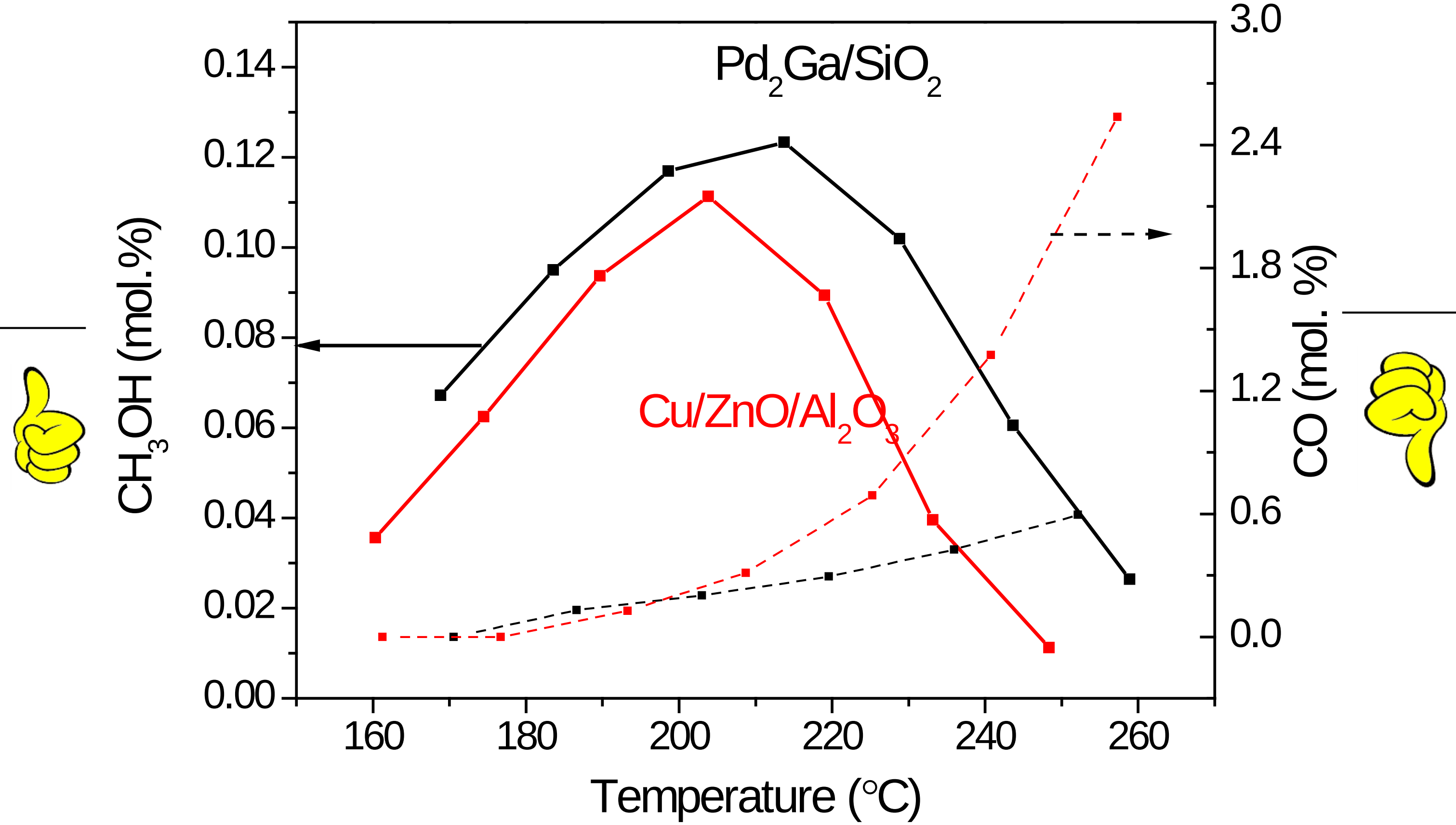
$$CO + 2H_2 \leftrightarrow CH_3OH$$

$Cu/ZnO/Al_2O_3$

- Very active, selective and cheap
- High pressure operations (50-100 bar)
- Suffers from sintering

1. Catalytic test

1 bar, 25% CO_2 and 75% H_2



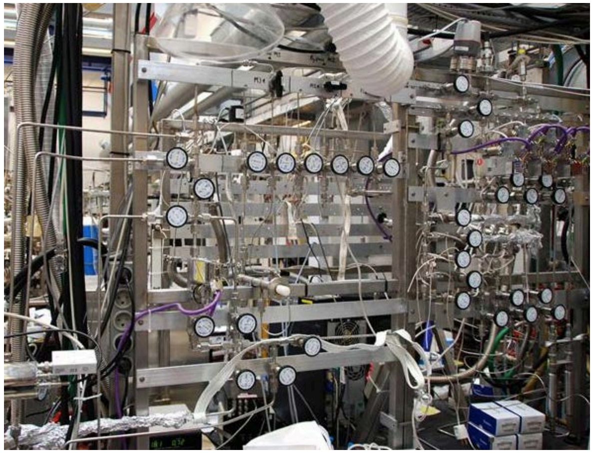
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

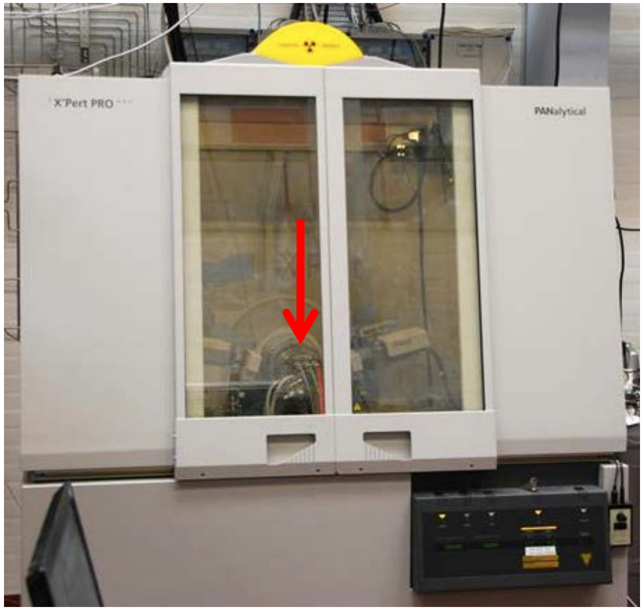
C. Baltes et al., "Correlations Between Synthesis, Precursor, and Catalyst Structure and Activity of a Large Set of CuO/ZnO/Al2O3 Catalysts For Methanol Synthesis". JOURNAL OF CATALYSIS 258.2 (2008): 334-344.

2. *In situ* XRD

Gas system

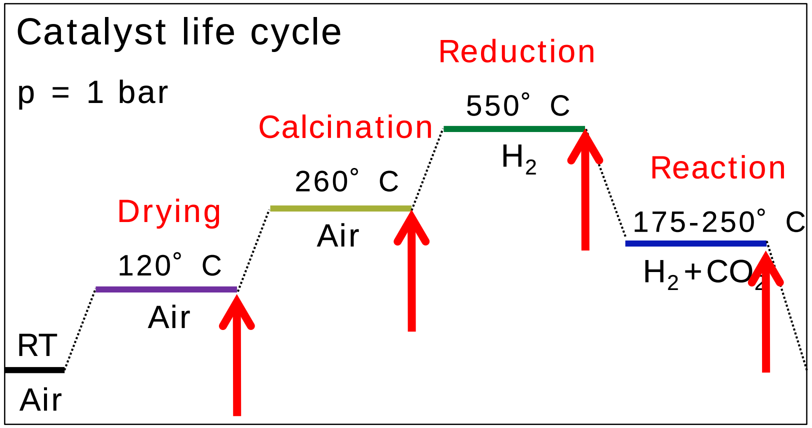


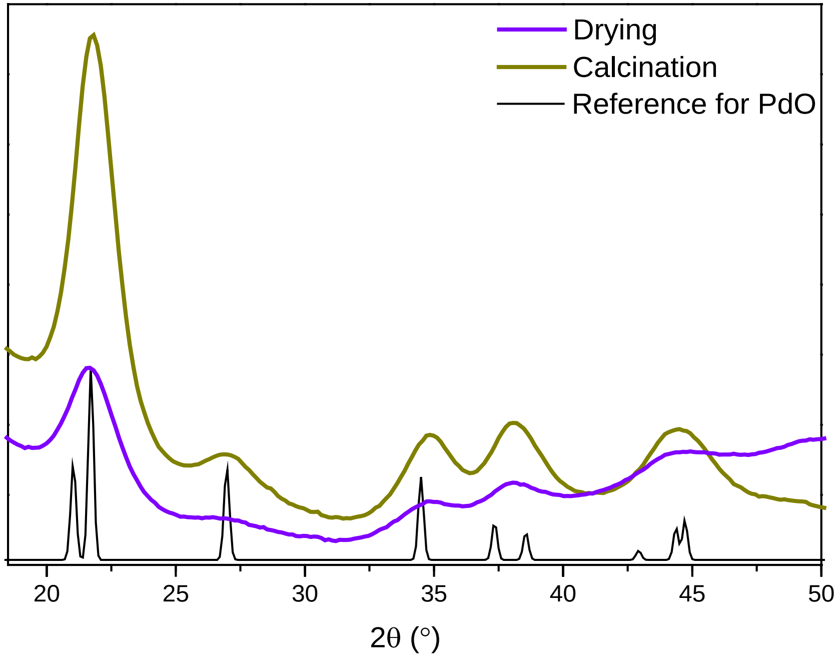
PANalytical X'Pert PRO

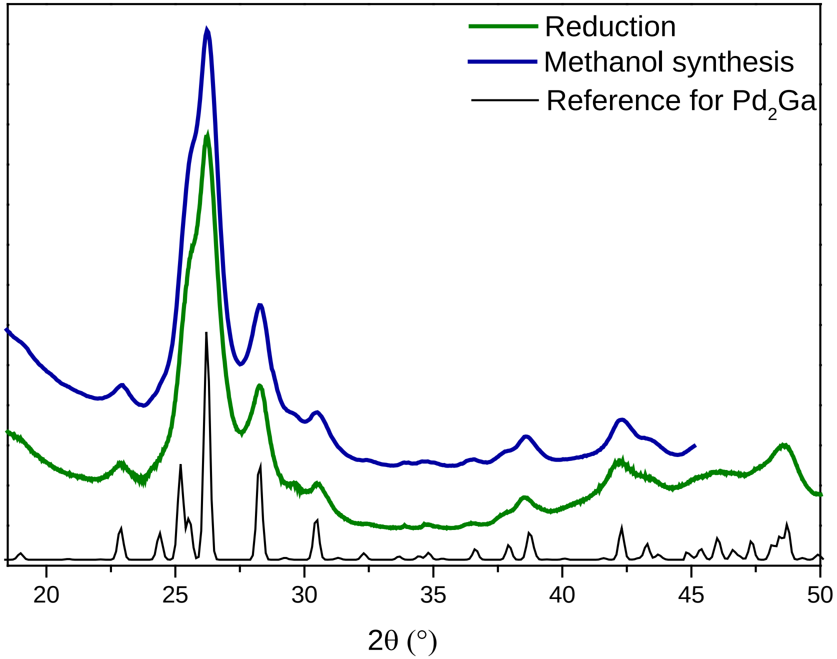


Anton Paar XRK 900

2. In situ XRD patterns

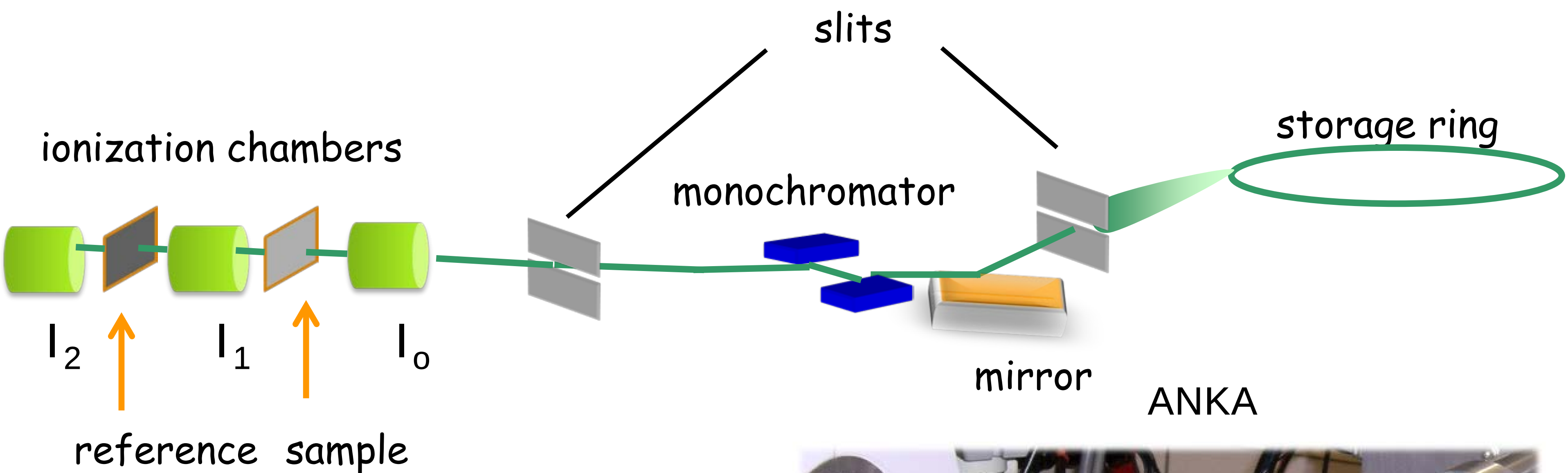




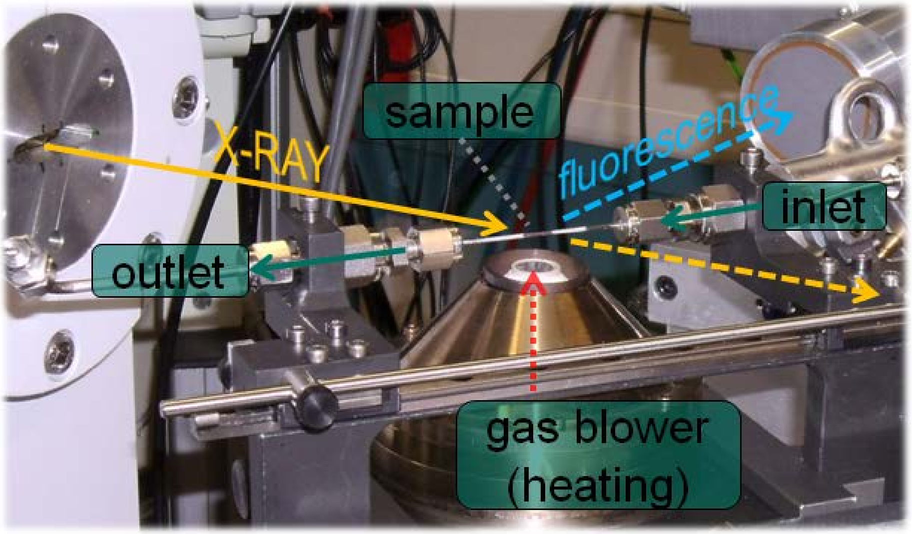


3. *In situ* EXAFS

Extended X-ray Absorption Fine Structure (EXASF)

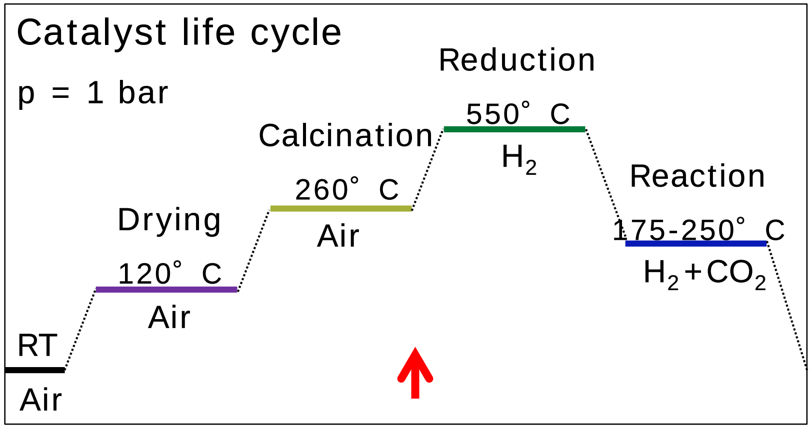


ANKA

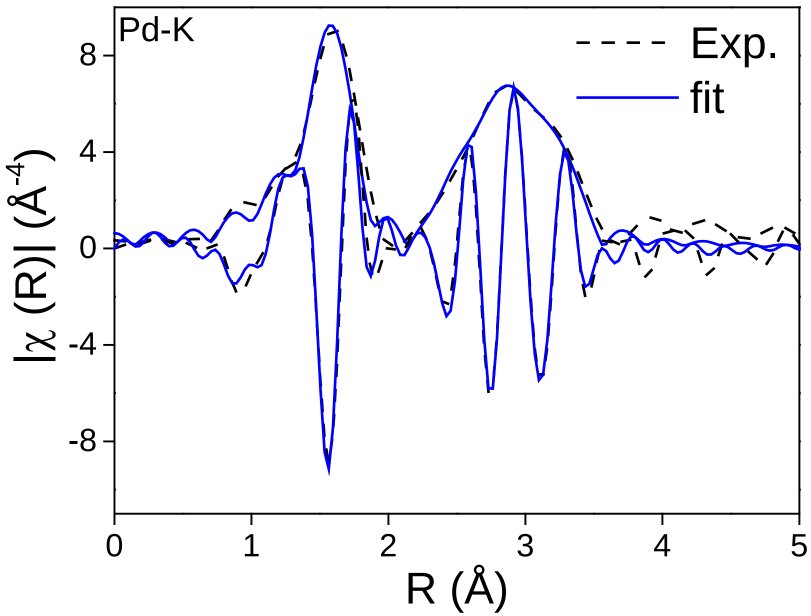


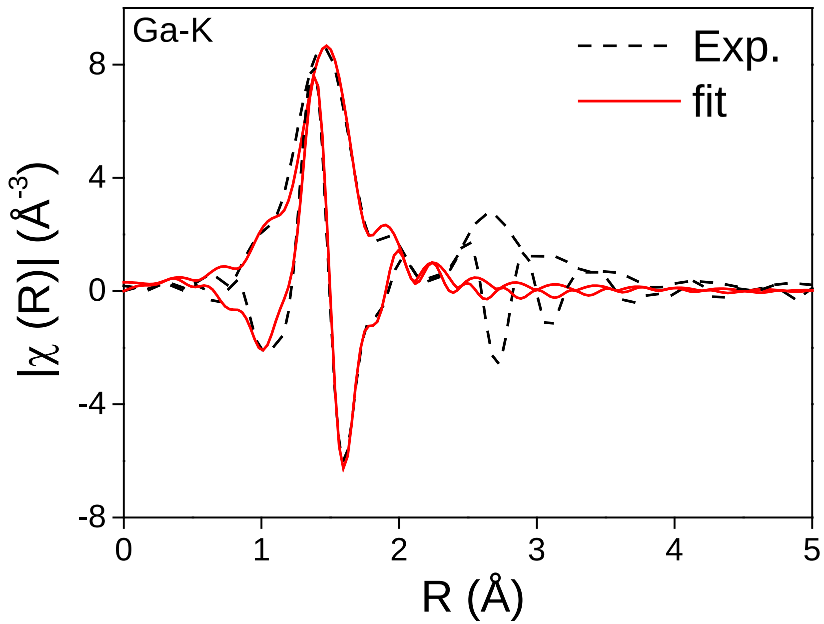
3. *In situ* EXAFS

H. W. P. Carvalho
J.-D. Grunwaldt



Edge	*Shell*	*atom*	*N*	*r(Å)*	*σ^2(10^{-3} Å^2)*	*ρ (%)*
Pd K	1st	O	4[f]	2.01[a]~	2.5 ± 0.7[a]	2.8
	2nd	Pd	4[f]	3.03[a]~	6.5± 0.8[a]	
	3rd	Pd	6.8±1.7[a]	3.42±0.01[a]	8.3± 1.8[a]	
Ga K	Tet.	O	2.9± 0.3[a]	1.90±0.02[a]	2.8 ± 1.9[a#]	1.2
	Oct.	O	1.5± 0.3[a]	2.07±0.04[a]	2.8 ± 1.9[a#]	





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H. W. P. Carvalho
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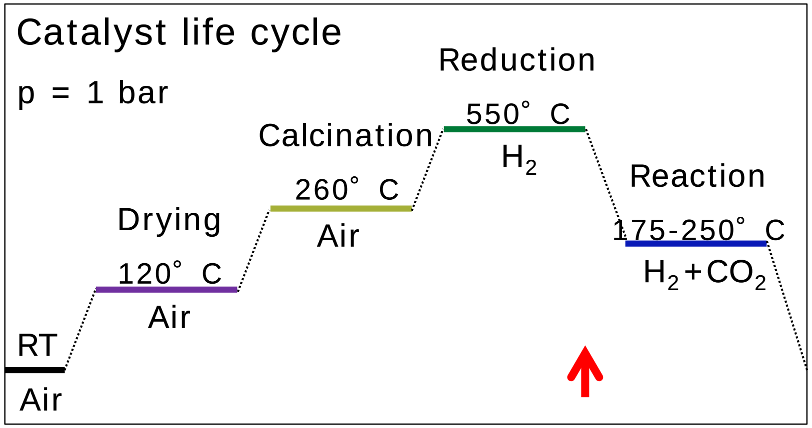
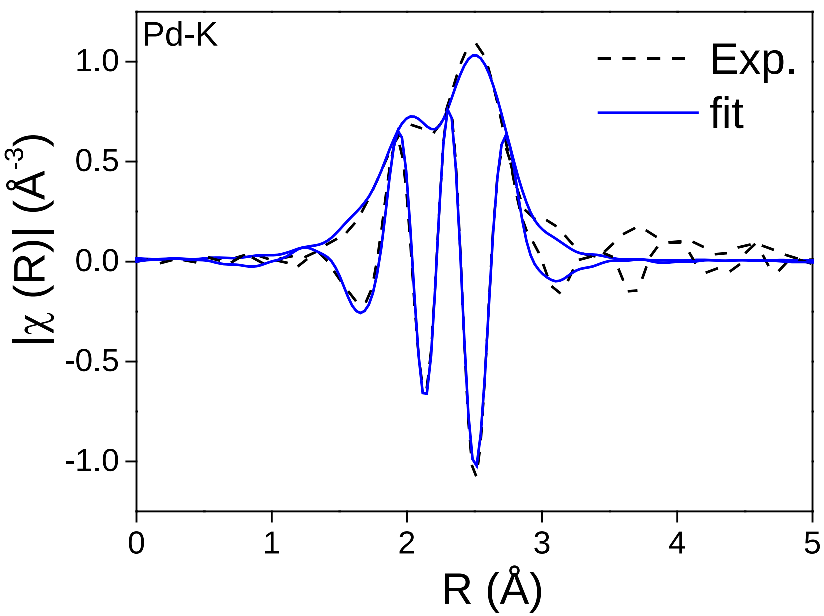
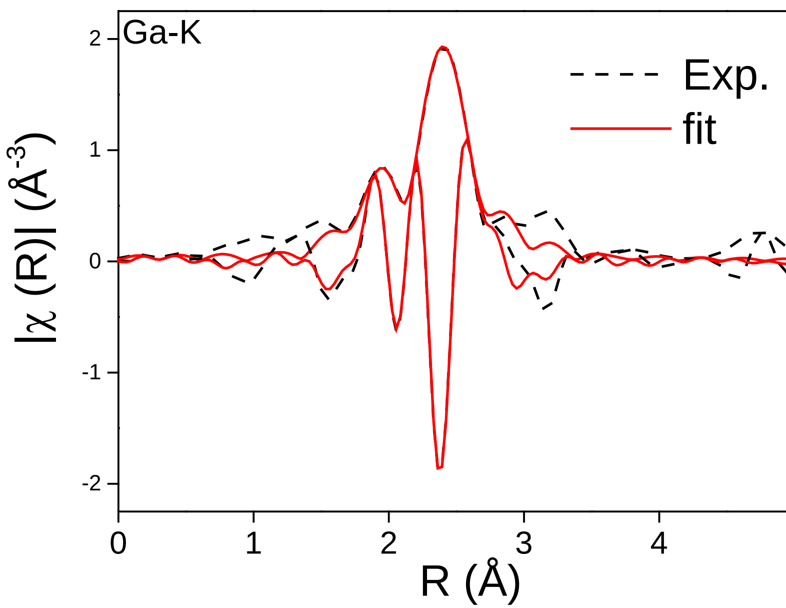


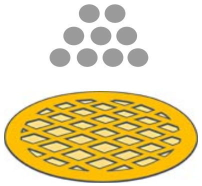
Edge	*Shell*	*atom*	*N*	*r(Å)*	*σ^2(10^{-3} Å^2)*	*ρ (%)*
Pd K	1st	Ga	2.8±0.5[a]	2.52±0.01[a#]	6.5 ± 0.6[a#]	2.5
	2nd	Pd	7.5± 1.4[a]	2.81±0.02[a]	11.4± 2.0[a]	
Ga K	1st	Pd	5.6± 0.3[a]	2.52±0.01[a#]	6.5 ± 0.6[a#]	

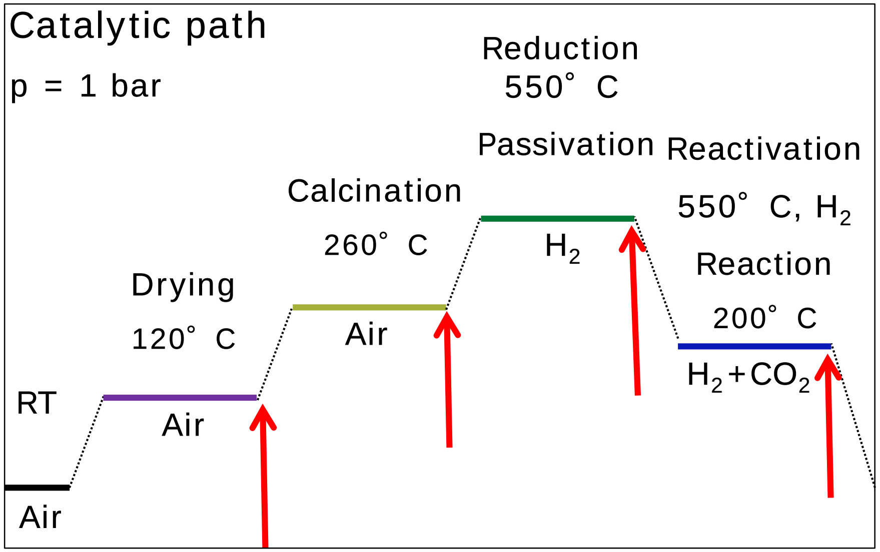




4. IL TEM

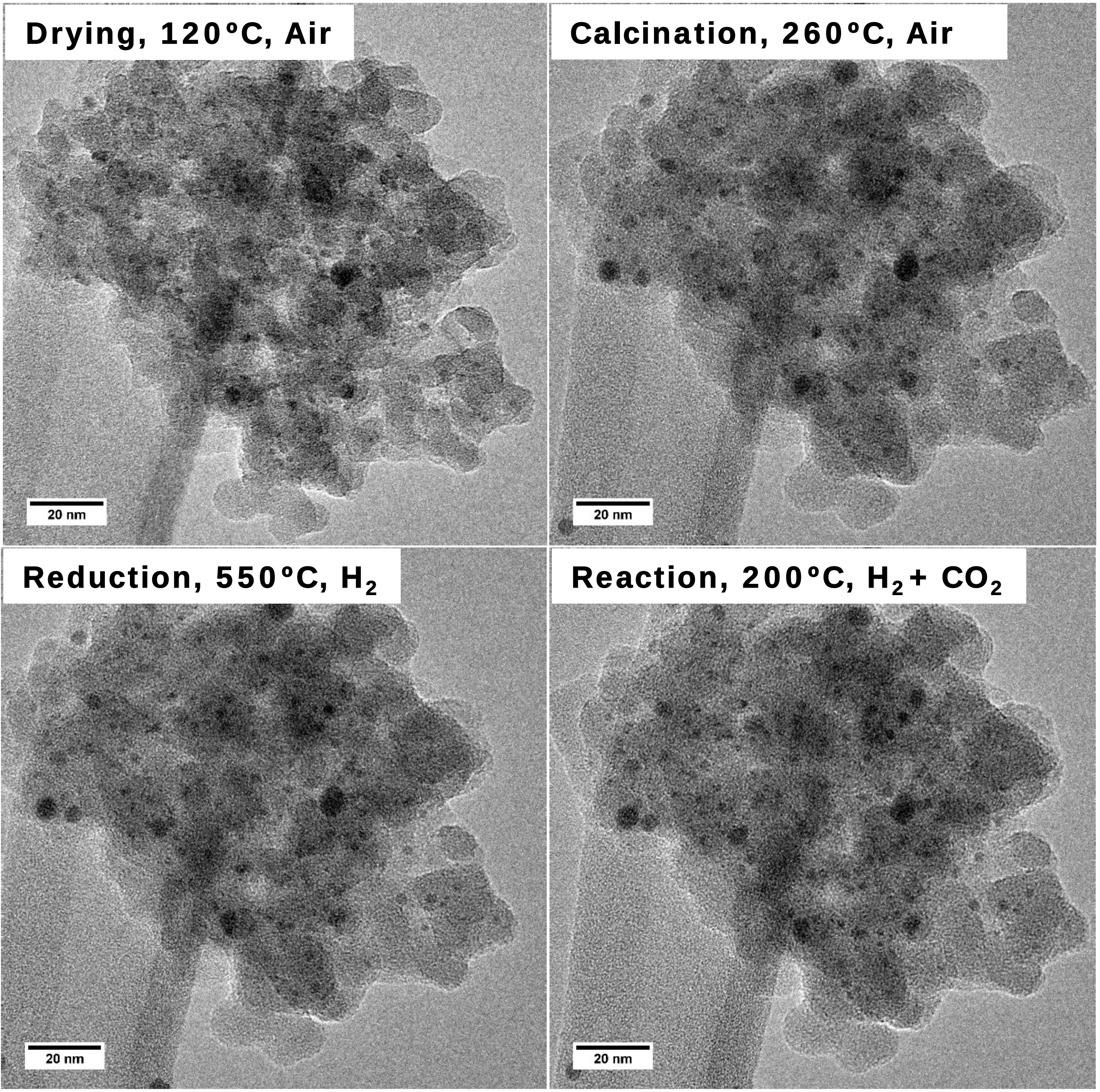
Deposition on Au/SiO_2 grid of RT dried precursor powder





Furnace ↔ TEM transfer of grids in air

4. IL TEM images

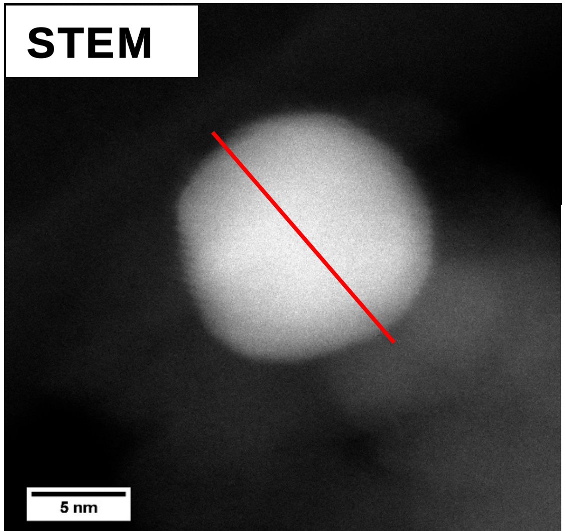


SIZE and DISPERSION

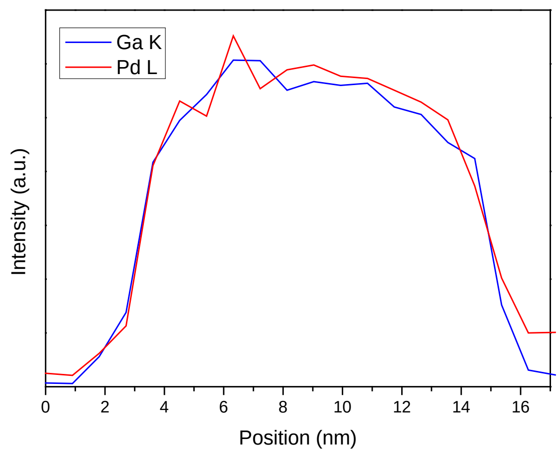
- Nanoparticles decorate the support after drying of the precursors.
- After calcination a sintering of the substrate is observed.
- The nanoparticles size and dispersion are determined upon calcination.
- No significant changes are observed after reduction and CO_2 hydrogenation to methanol.

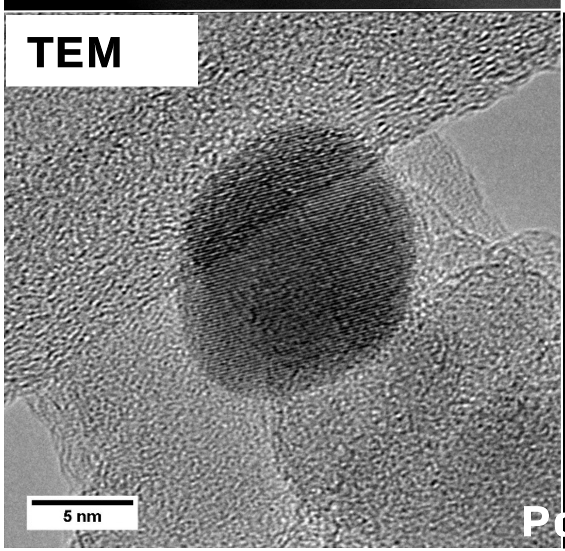
4. IL TEM analysis

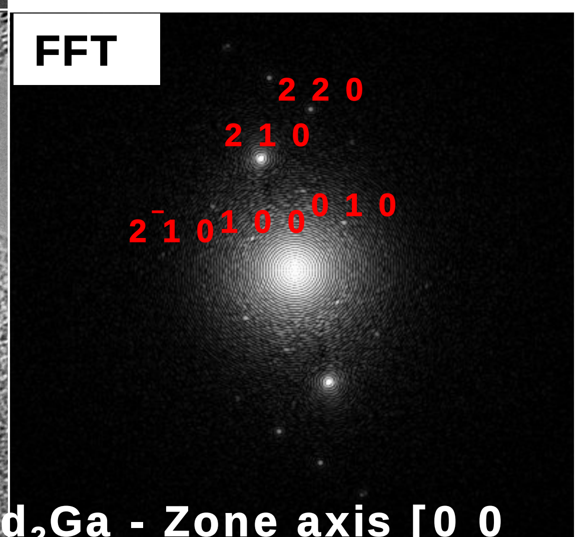
After Reduction, passivation, exposure to air



EDX line profile





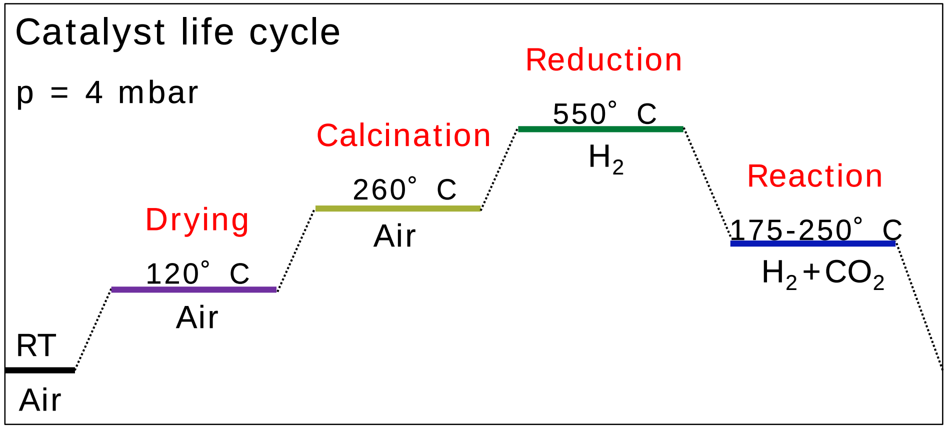


COMPOSITION and CRYSTAL STRUCTURE

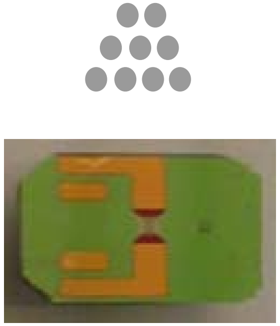
- No segregation of Pd and Ga is observed:
  the bulk structure of the particle is maintained after exposure to air.
- FFT reveals the crystal structure of a Pd_2Ga nanoparticle.
- Hints of a surface oxide layer.

5. ETEM

Titan, FEI



Deposition on Holey Au/C grid of RT dried precursor powder



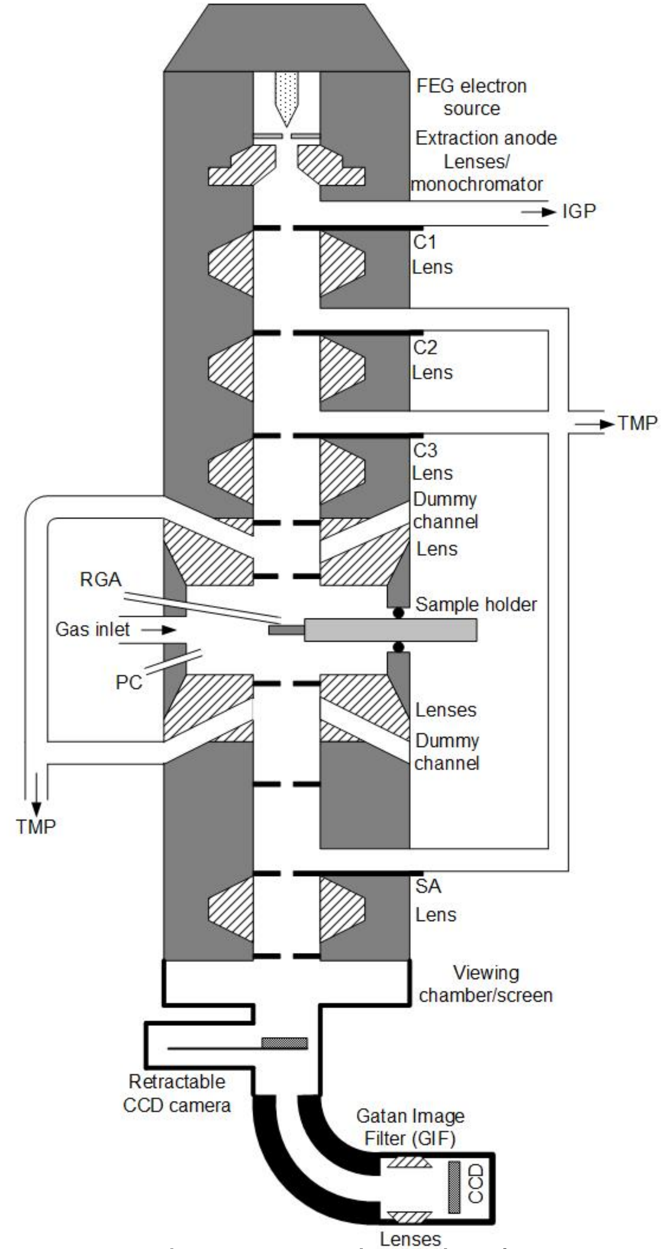
Deposition on Protochips

5. ETEM

- Monochromated FEG electron source

- Differential pumping system
  1. Gas is leaked in
  2. First set of diffusion limiting apertures
  3. Turbo molecular pump
  4. Second set of diffusion limiting apertures
  5. Turbo molecular pump
  6. Ion getter pump (IGP)

- Direct line of sight!

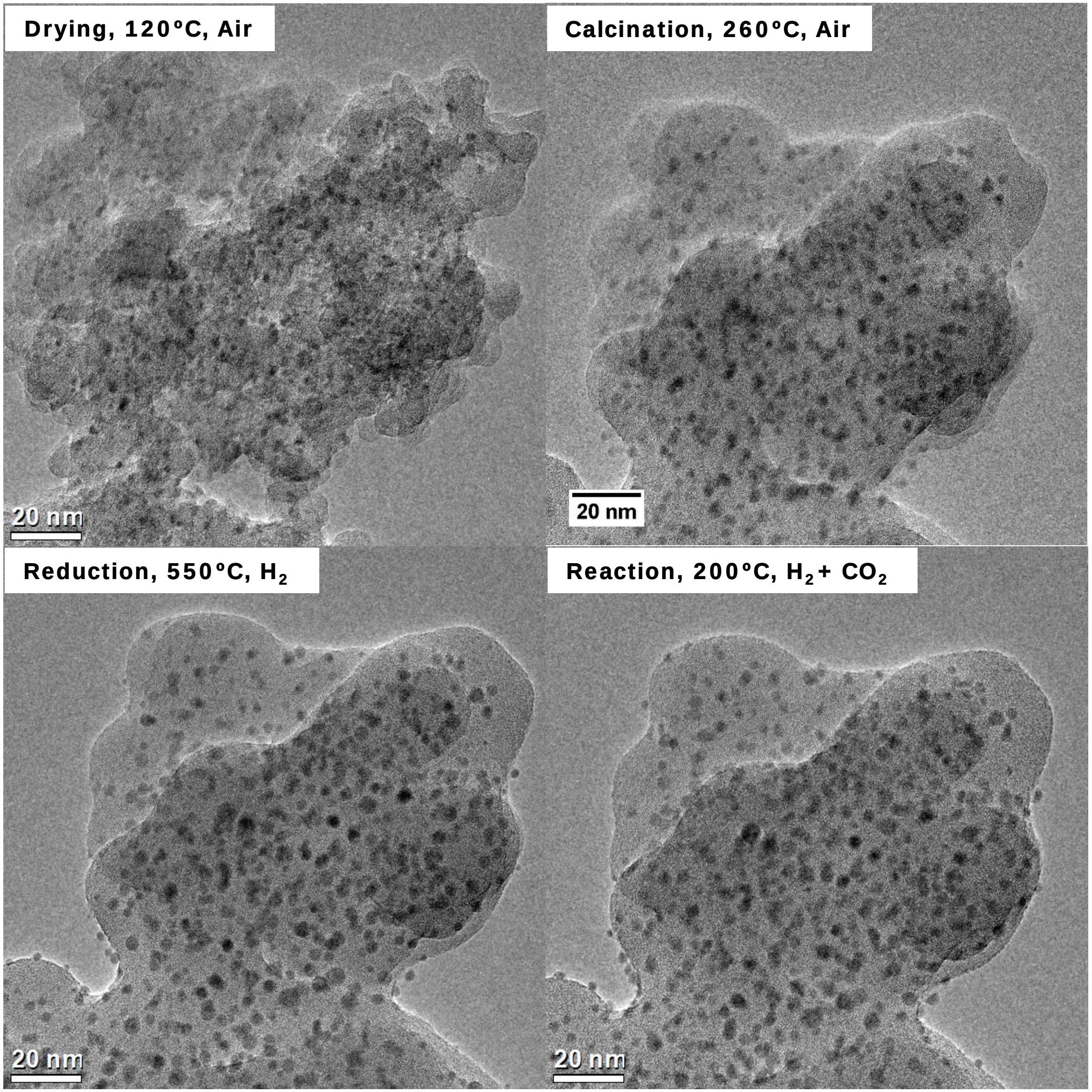


T.W. Hansen, J.B. Wagner *et al.*, Mater. Sci. Technol. 26, 1338 (2010)

5. ETEM – conditions

- Orders of magnitude
  - Conventional TEM ~10^{-8}mbar
  - Environmental TEM ~10^{1}mbar
  - Closed Cell ETEM ~10^{3}mbar
  - Bench scale reactors ~10^{3}mbar
  - Industrial reactors ~10^{5}mbar
- We have gone most of the way…

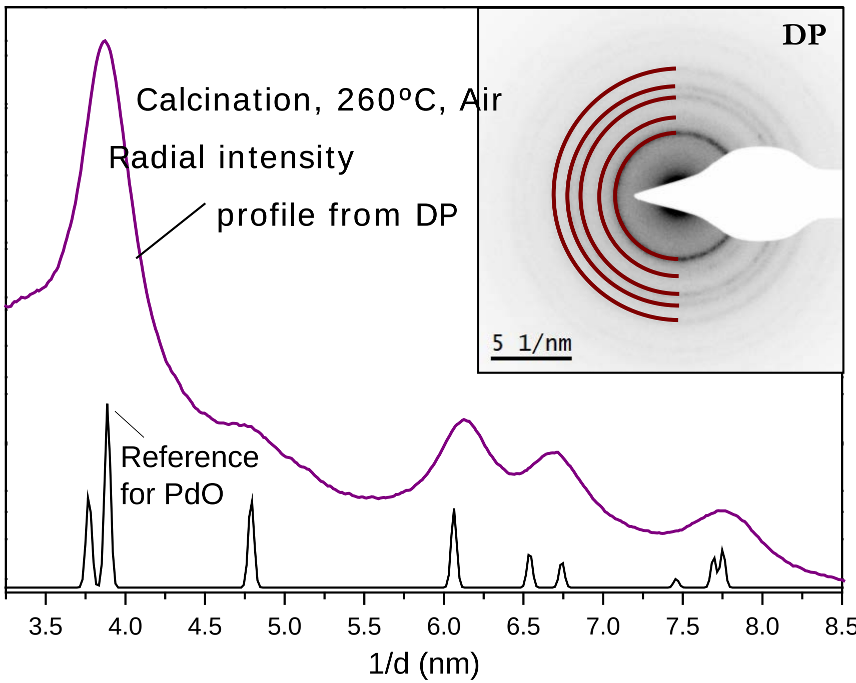
5. ETEM images

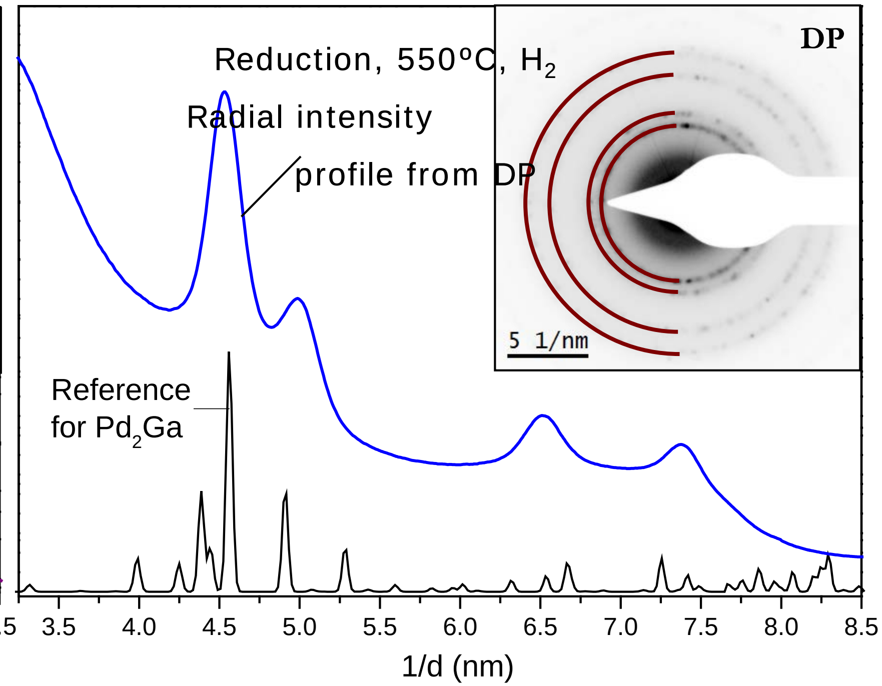


SIZE and DISPERSION

- Nanoparticles decorate the support after drying of the precursors.
- After calcination a sintering of the substrate is observed.
- Size and dispersion are determined upon calcination.
- No significant changes are observed after reduction and methanol synthesis.
- ETEM results correlates with the 1 bar treated catalyst.

5. SAED patterns

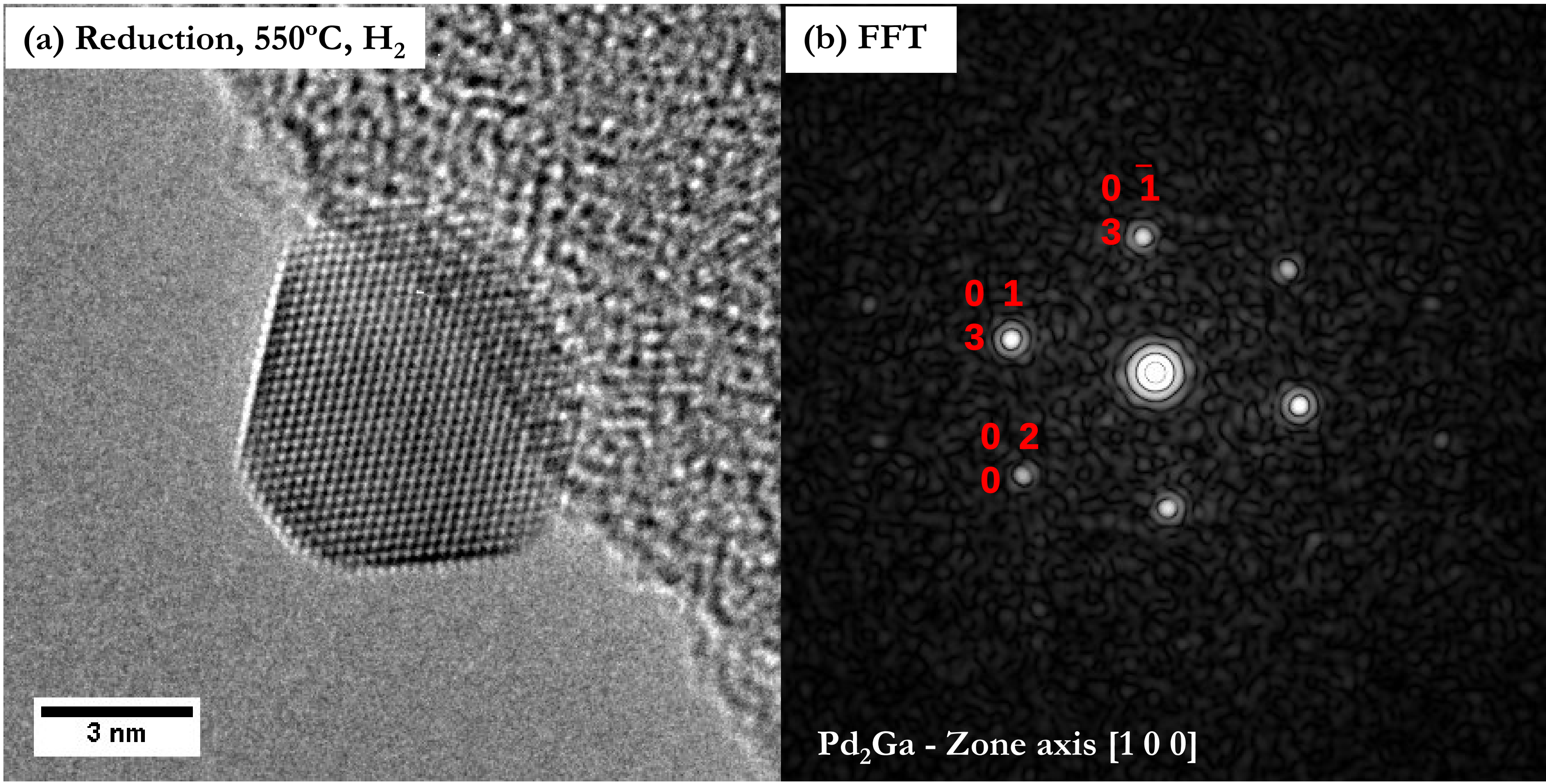




- PdO phase is observed after calcination.
- Pd_2Ga phase is formed upon reduction.

ETEM (4 mbar) and XRD (1 bar) correlates

6. HRTEM



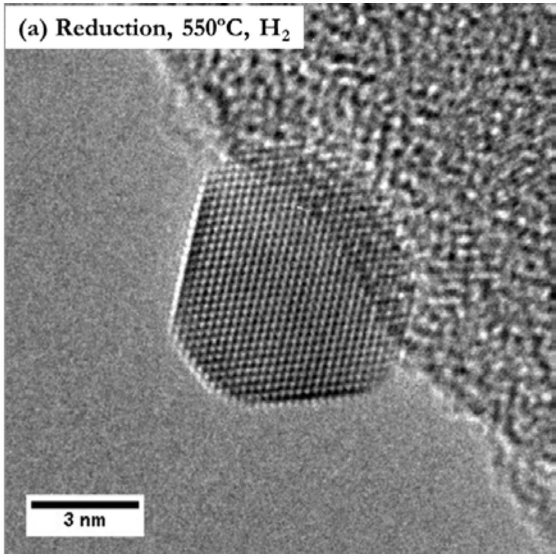
(a) Reduction, 550ºC, H_2
3 nm
(b) FFT
$0\ \bar{1}\ 3$
$0\ 1\ 3$
$0\ 2\ 0$
Pd_2Ga - Zone axis [1 0 0]

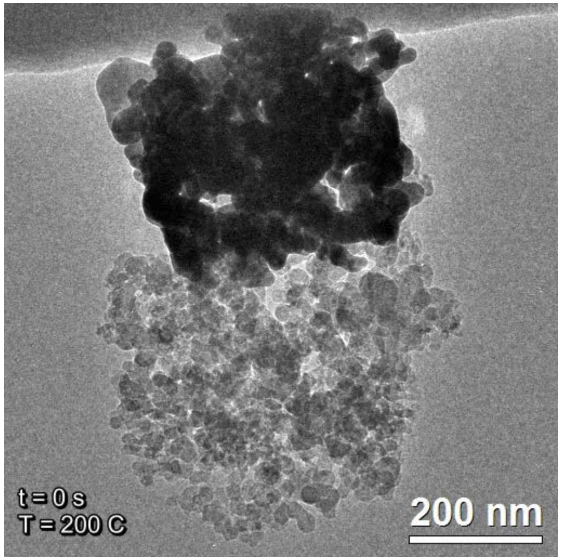
Paralle approach - Conclusions

- Pd_2Ga/SiO_2 catalyst is investigated by complementary techniques.
- The test of the catalyst shows that the methanol yield from Pd_2Ga/SiO_2 is higher to the one given by $Cu/ZnO/Al_2O_3$, while the CO yield is lower.
- XRD, EXAFS and SAED show that the Pd_2Ga phase is formed upon reduction and is stable with methanol synthesis.
- IL-TEM and ETEM images show that particles size and dispersion are determined upon calcination and no significant changes are observed after reduction and methanol synthesis.
- ETEM results are representative of the 1 bar pressure treated catalyst, closing the pressure gap between techniques.
- Further investigation is required in order to further optimize the catalyst and better understand the alloy formation mechanism.

Outline

- The *in situ* toolbox
  - Environmental TEM
- The catalysts life cycle - Identical location and ETEM
  - Intermetallic $GaPd_2/SiO_2$ nanoparticles for low pressure CO_2 hydrogenation to methanol
- Watching the reaction - ETEM
  - Soot oxidation by Ag
- Summary and acknowledgement





Watching the reaction

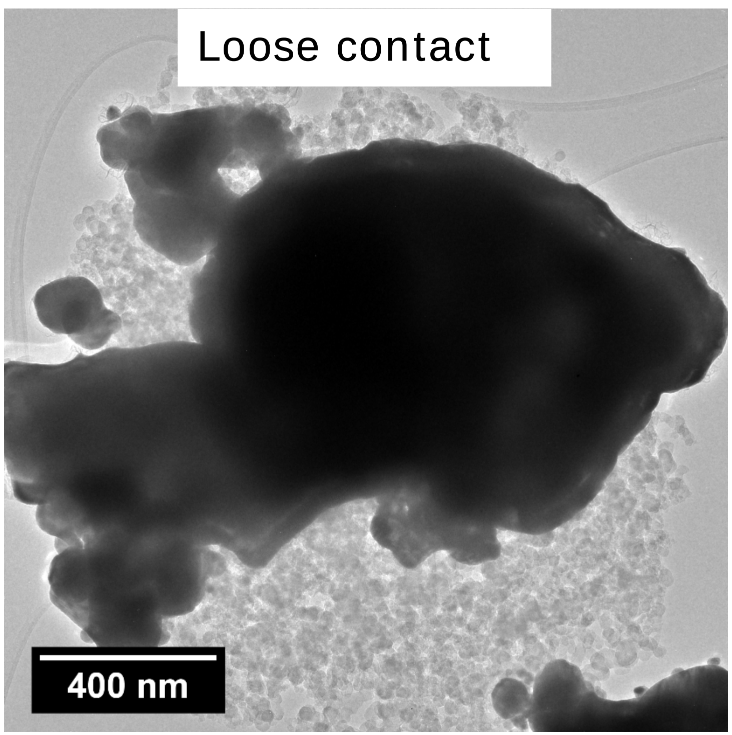
Soot oxidation by Ag

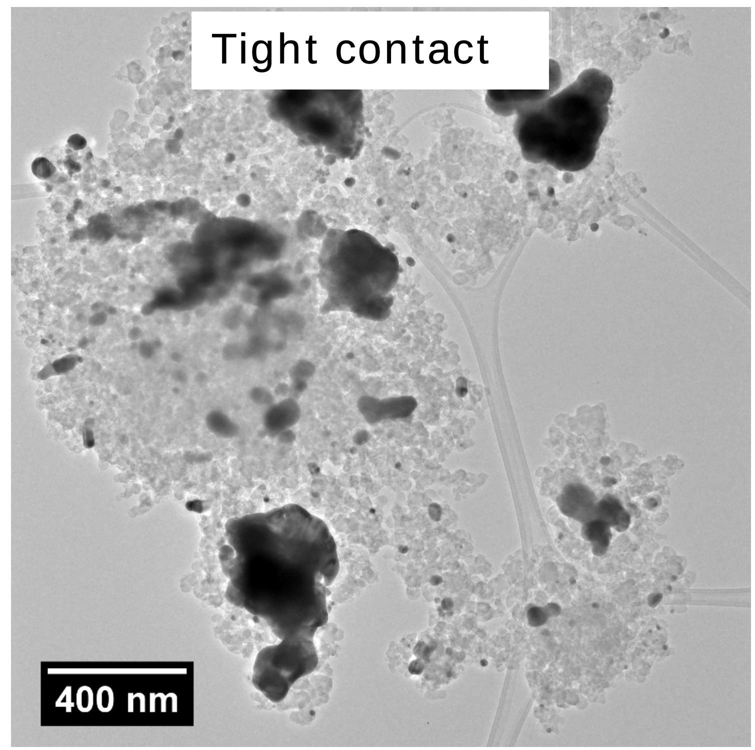
Dr. Diego Gardini

Soot oxidation by Ag catalyst

- Remove soot particles in exhaust of diesel engines by filters for a cleaner and healthier environment

- Low temperature regeneration of filters to reduce fuel consumption

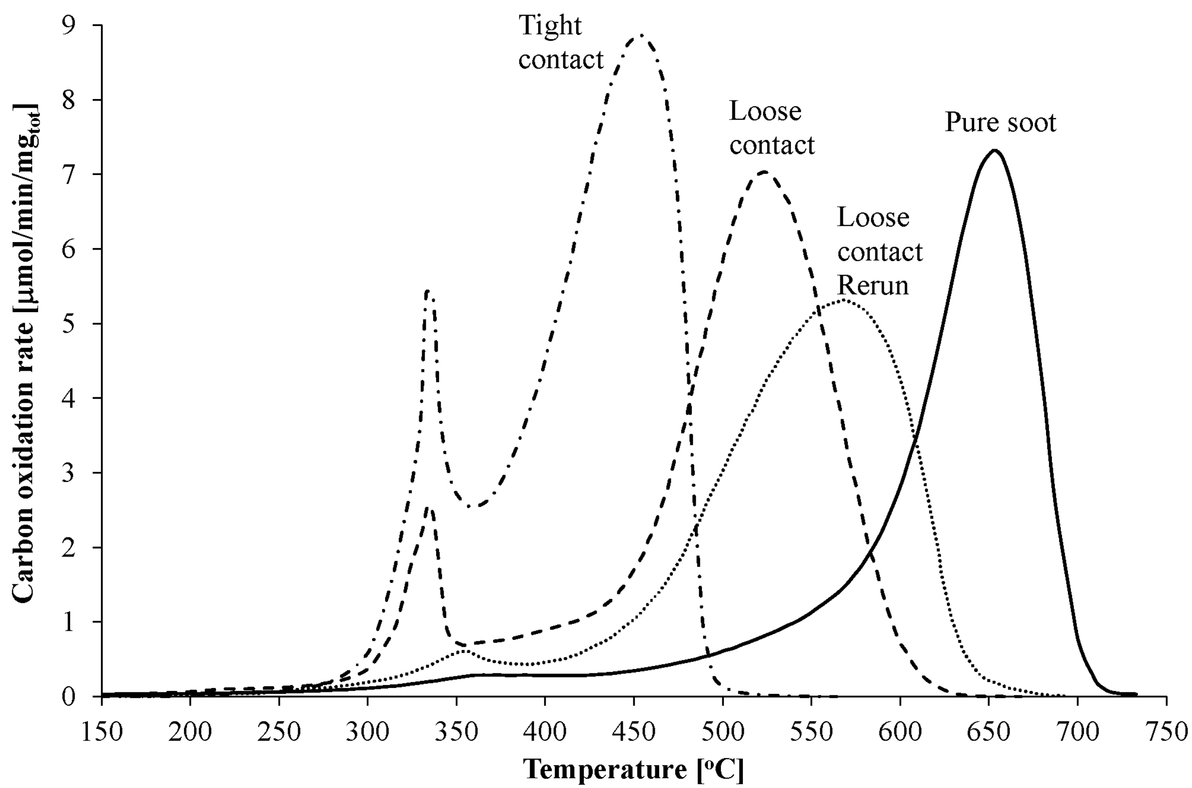




Gardini, JBW et al. submitted 2015

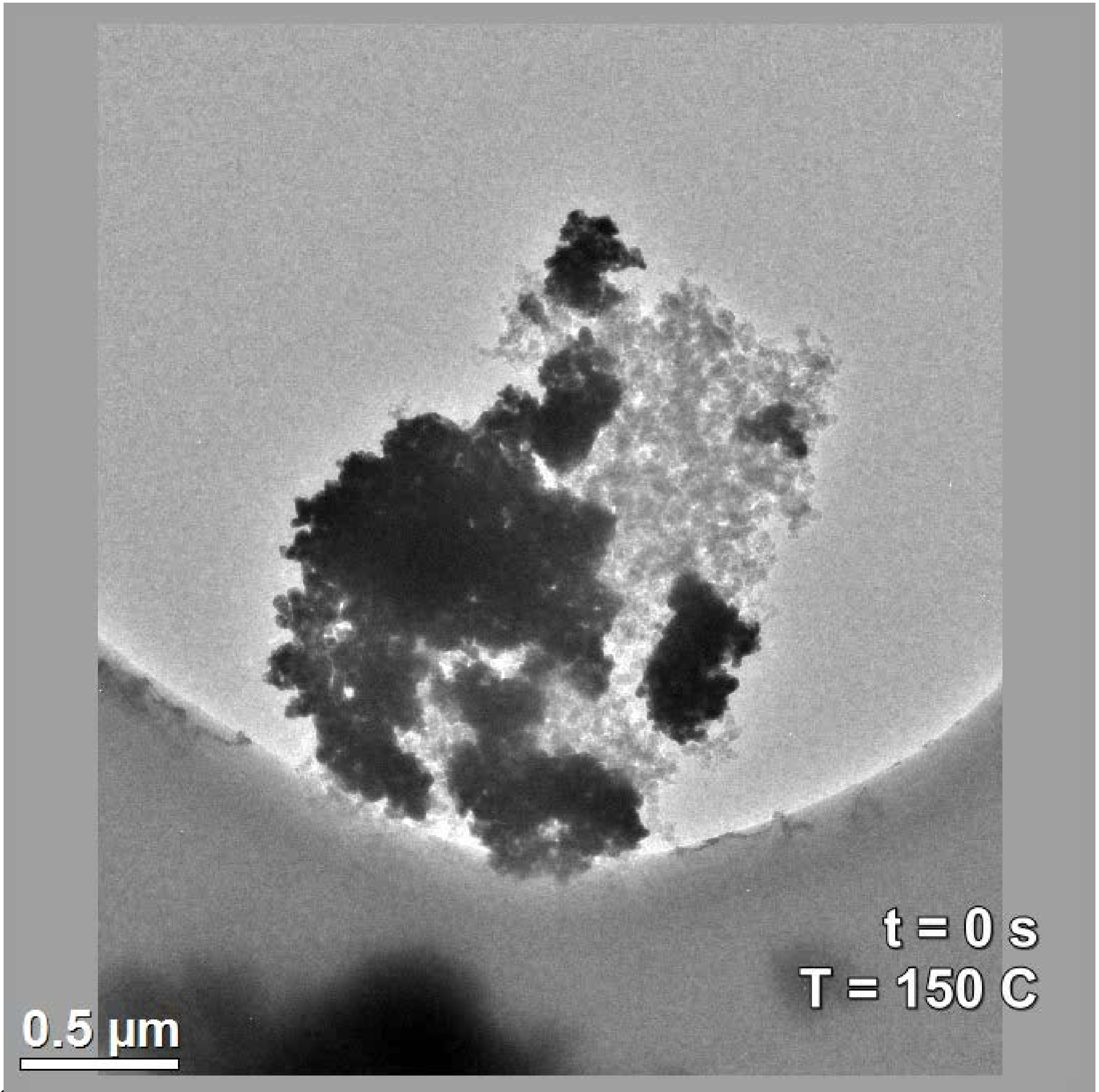
Silver Catalyst for Low Temperature Soot Oxidation

- Soot:silver= 1:5 wt:wt,
- Heating ramp = 11°C/min,
- 1 NL/min, 10.2 vol% O_2 in N_2.



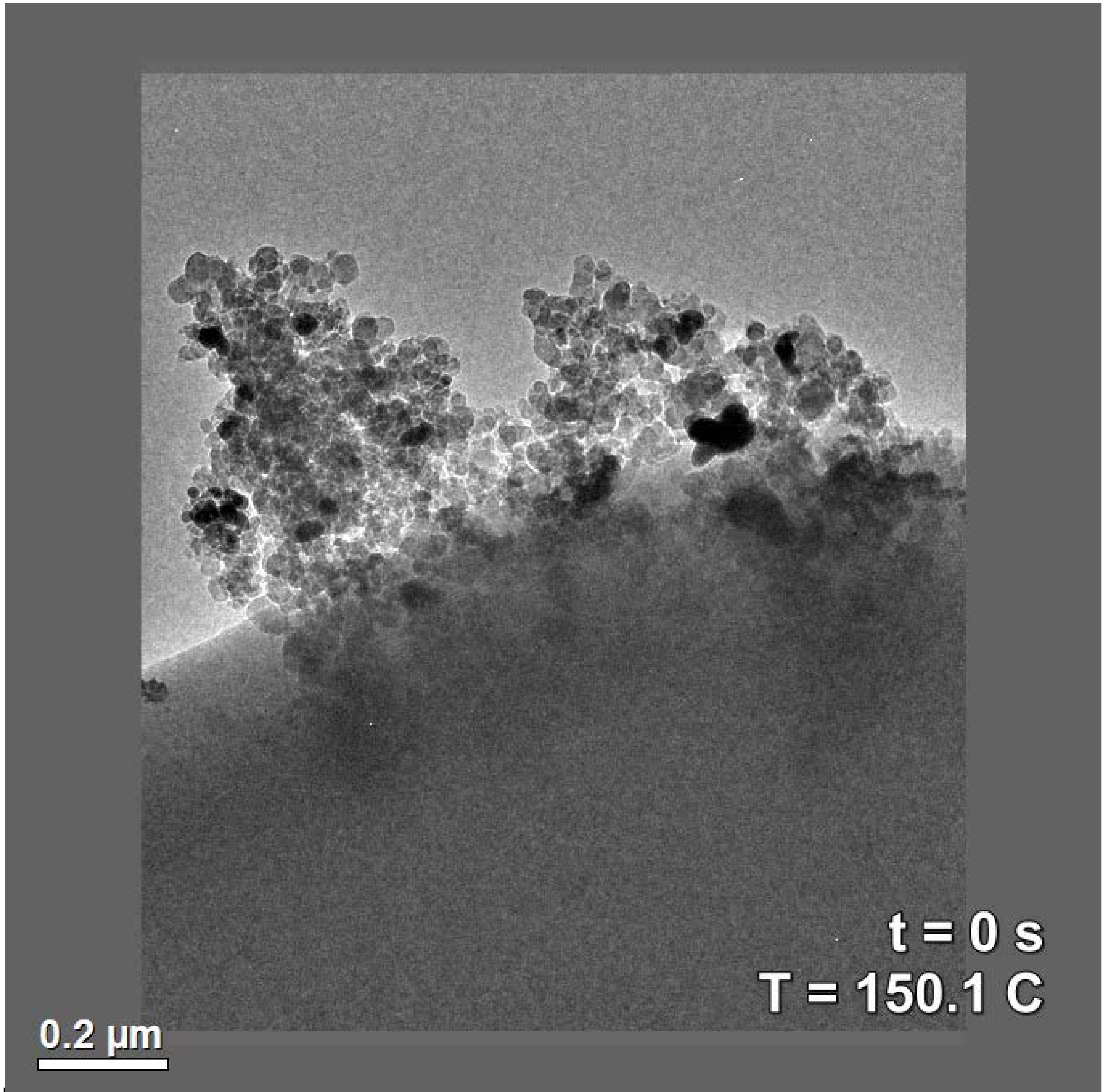
Loose contact

- $P = 300$ Pa O_2



Tight contact

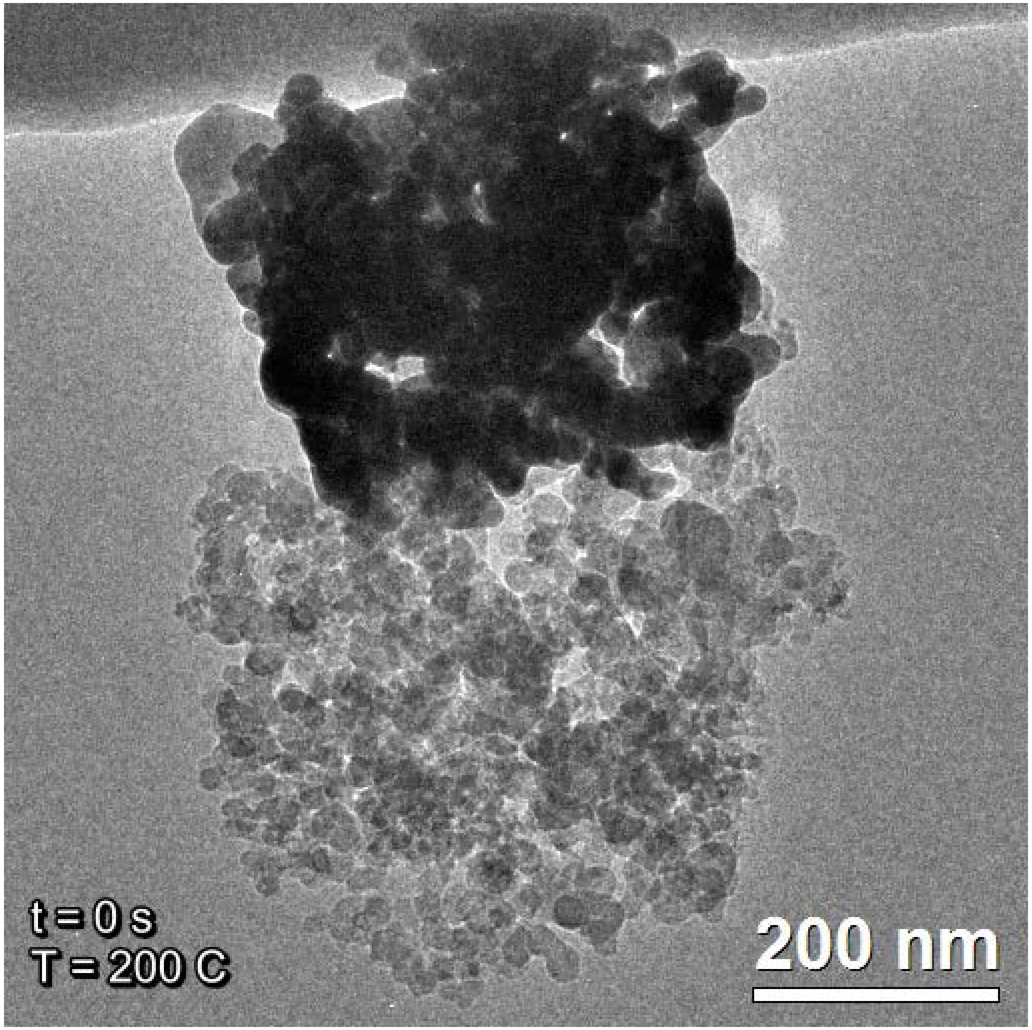
- $P = 300$ Pa O_2



Silver mobility on loose contact

- P=300 Pa O_2

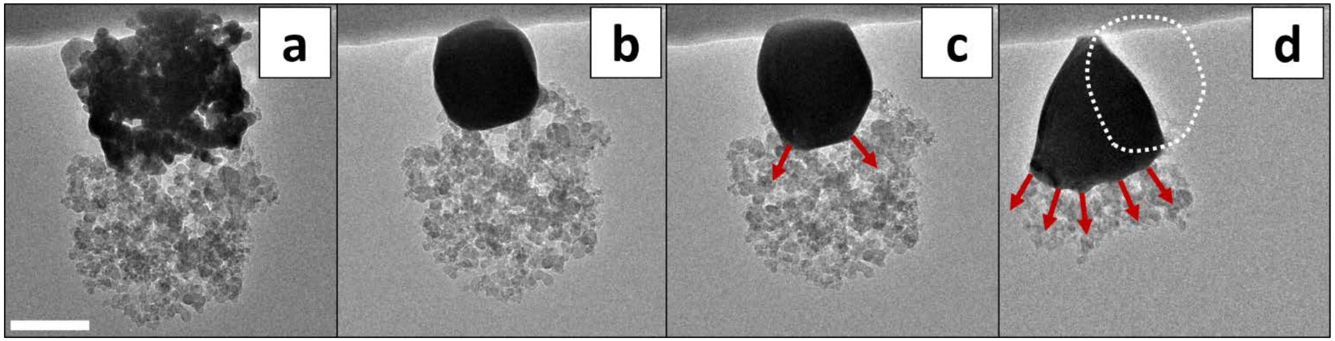
- Ag/soot interface increases during oxidation

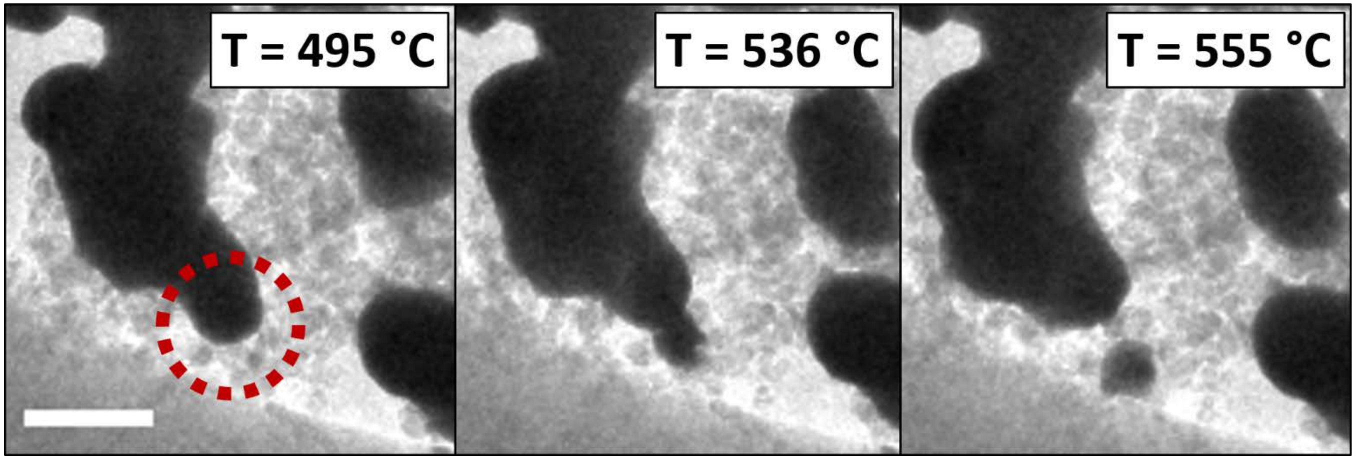


Gardini, JBW et al. submitted 2015

Silver mobility on loose contact

- Ag/soot interface increases during oxidation
- Ag detaches

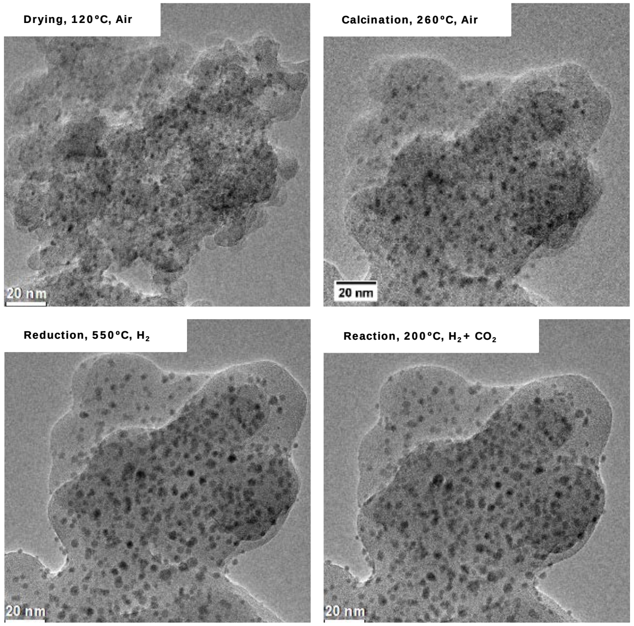




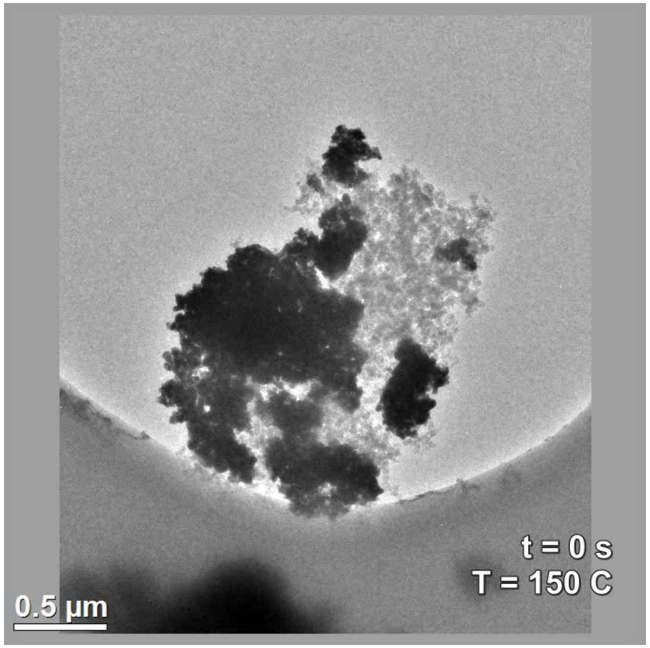
Gardini, JBW et al. submitted 2015

Summary

- Catalytic life cycle
  - Catalyst formation
  - Catalyst test



- Visualizing catalytic reaction
  - Soot oxidation



Acknowledgements

DTU Cen
Center for Electron Nanoscopy

Dr. Diego Gardini, Dr. Elisabetta Fiordaliso,
Prof. Jakob B. Wagner

DTU Physics
Department of Physics

Dr. Christian Fink Elkjær, Dr. Irek Sharafutdinov,
Prof. Ib Chorkendorff

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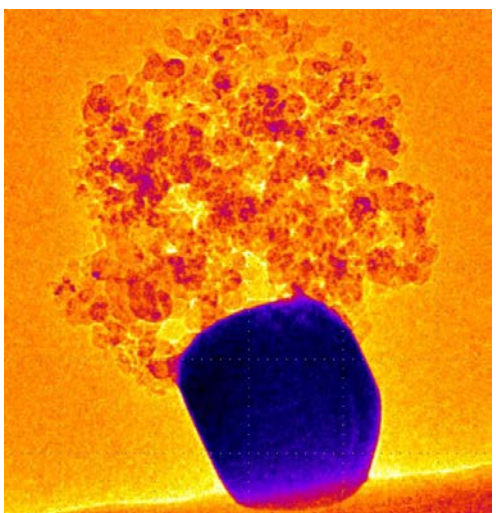
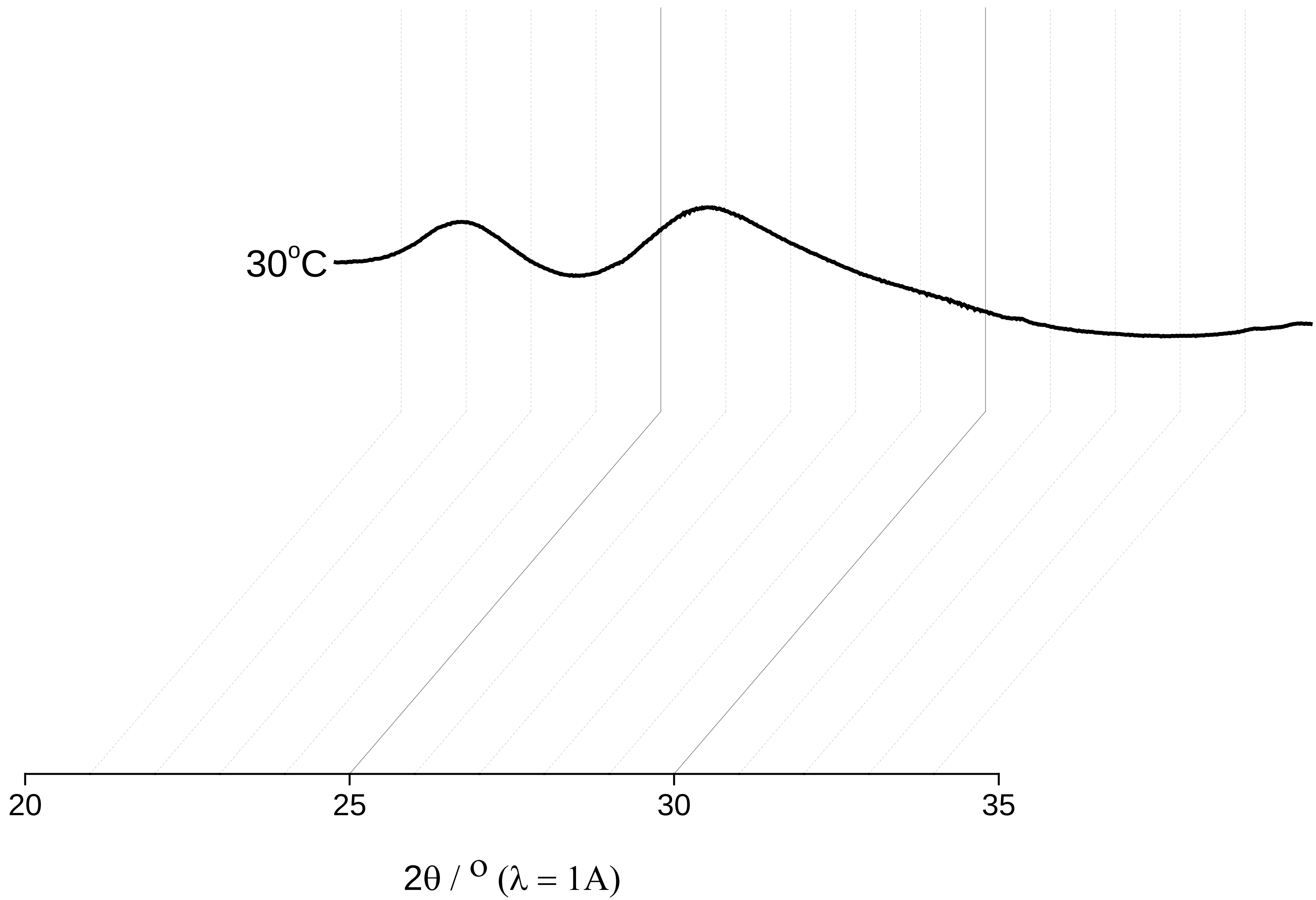
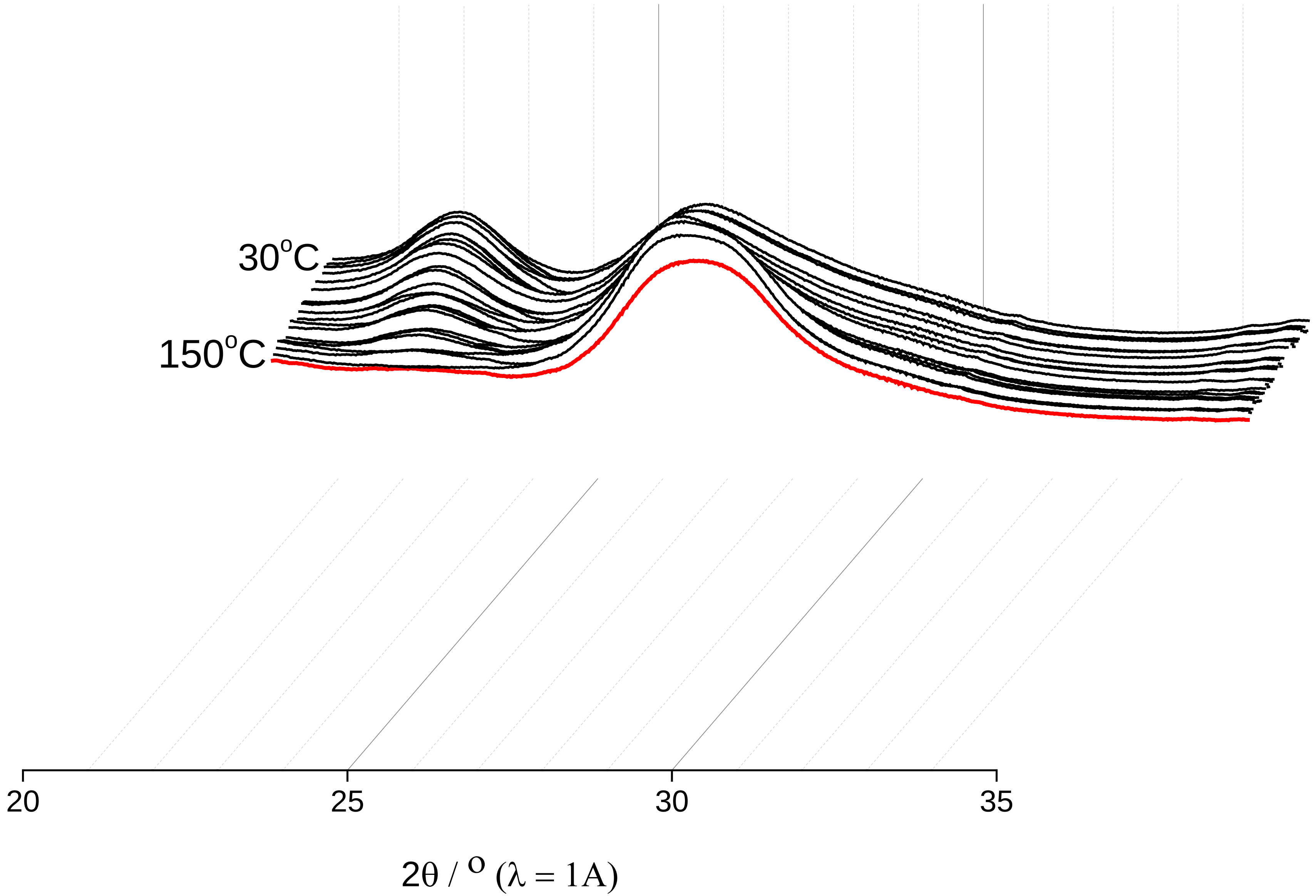


Additional info

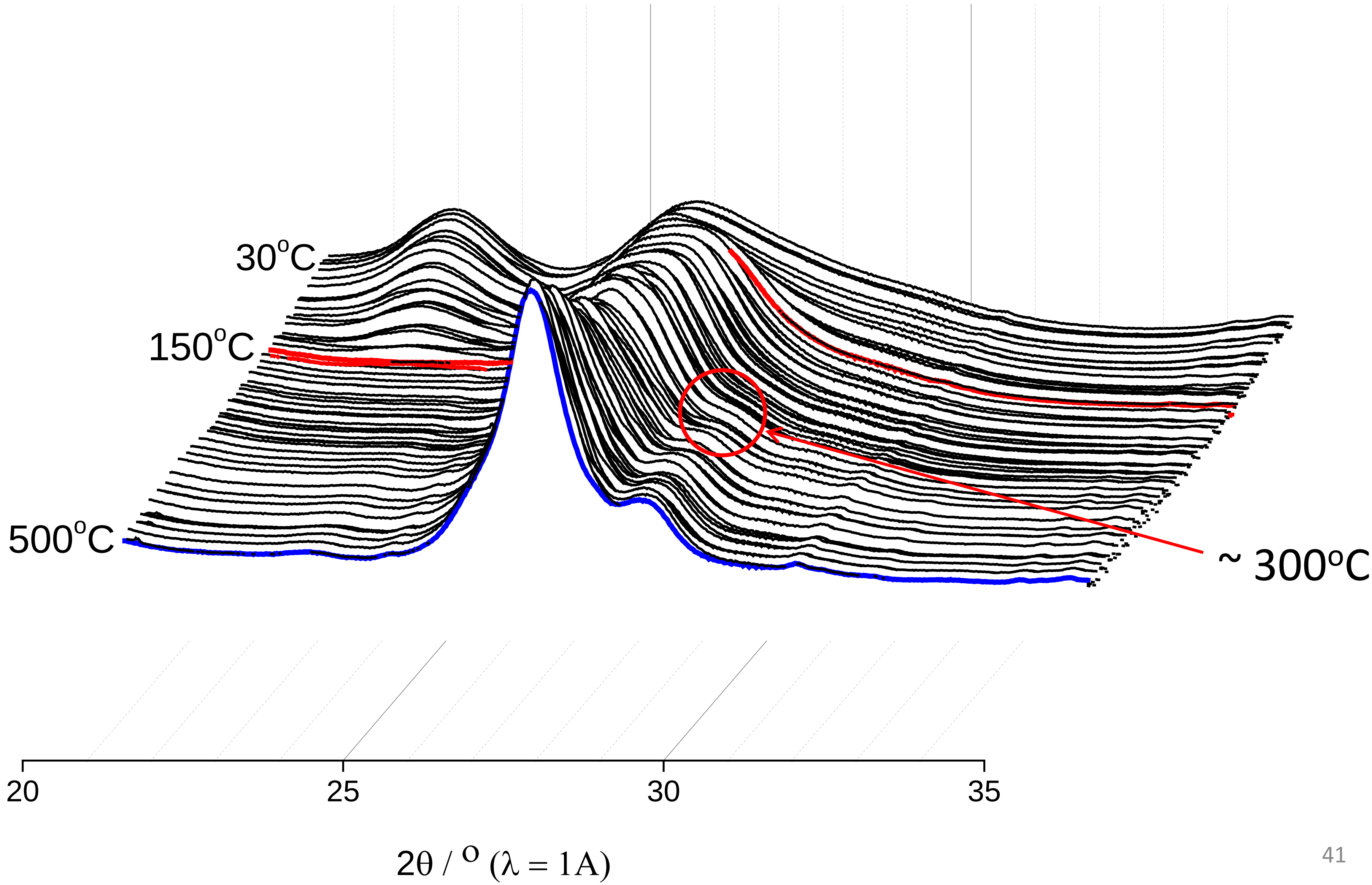
Starting phase after calcination – PdO (13 wt%)



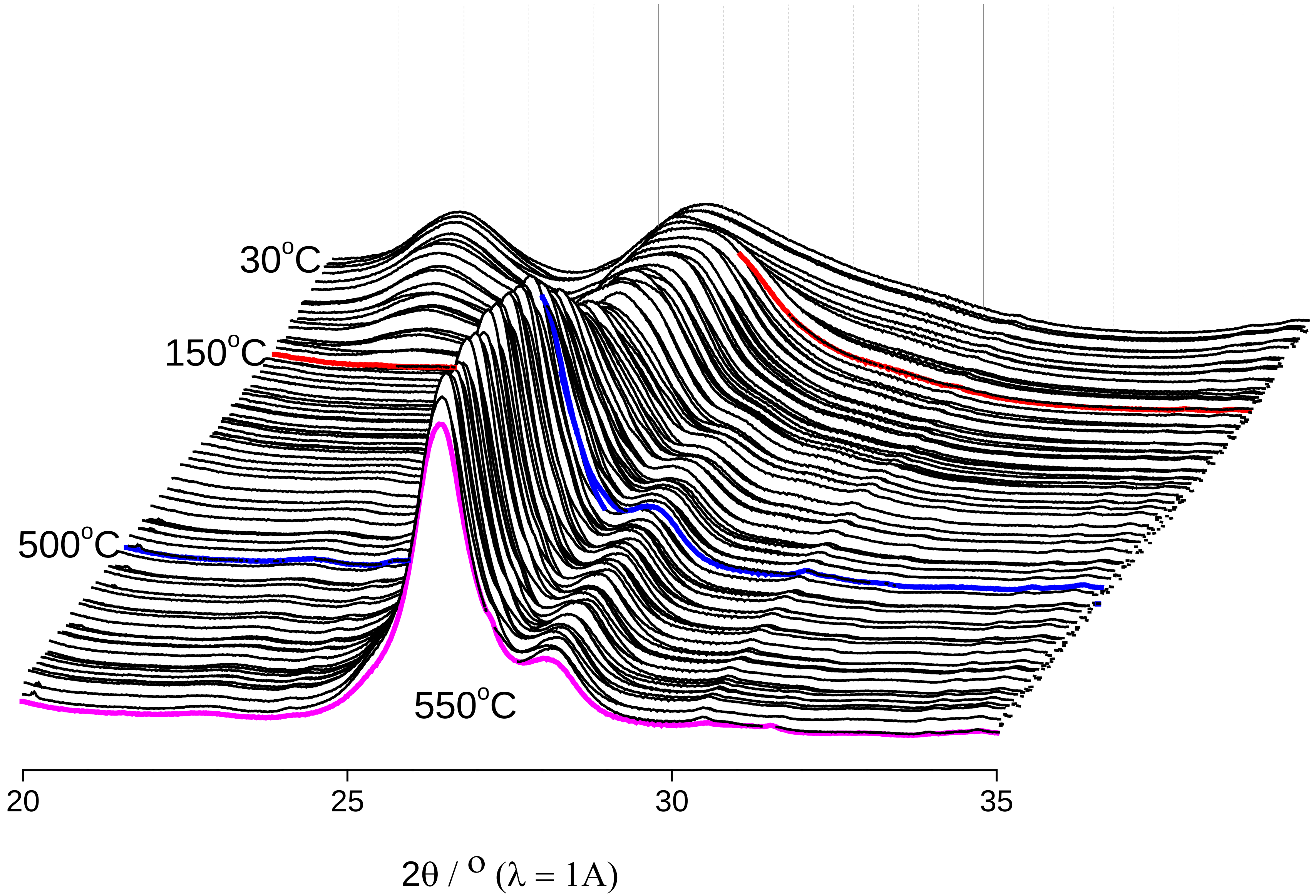
PdO transformed into Pd upon heating in H_2/Ar (13 wt%)



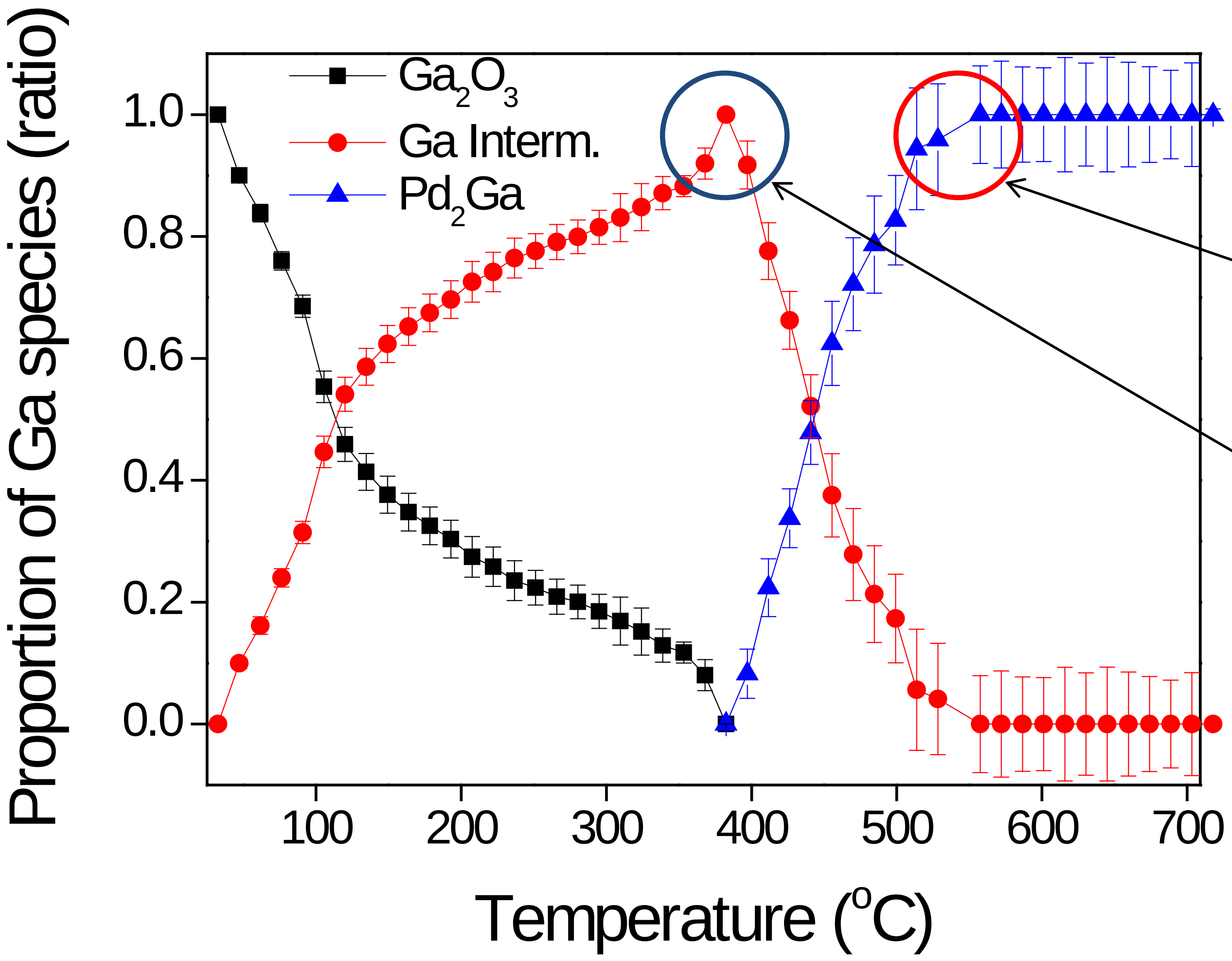
Pd is alloyed with Ga at T > 300^{o}C (13 wt%)



Alloying seems to be completed at T = 500°C (13 wt%)



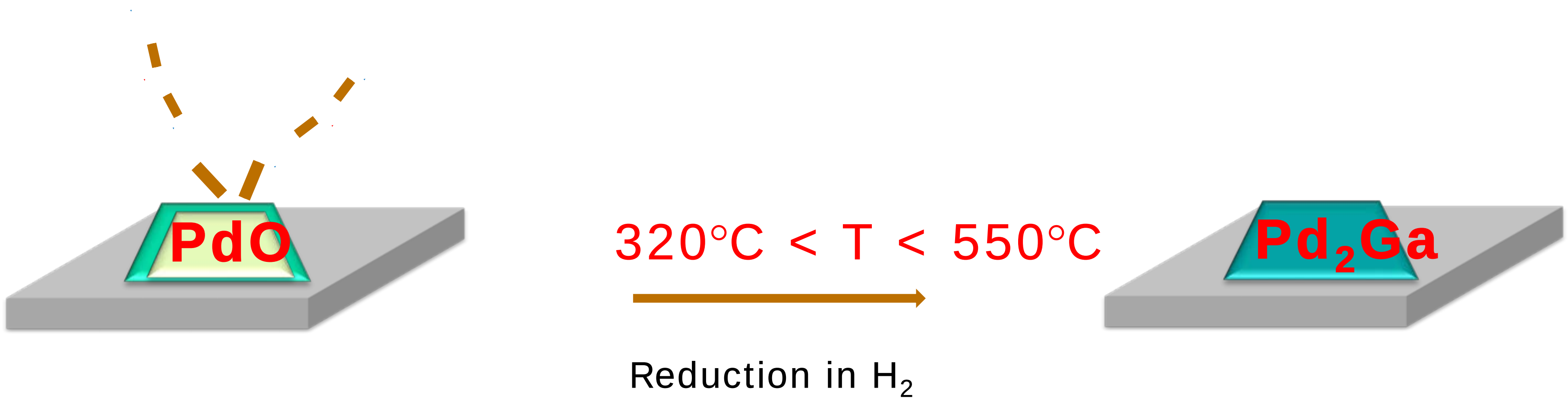
XAS – proportion of Ga species during TPR (23 wt%)



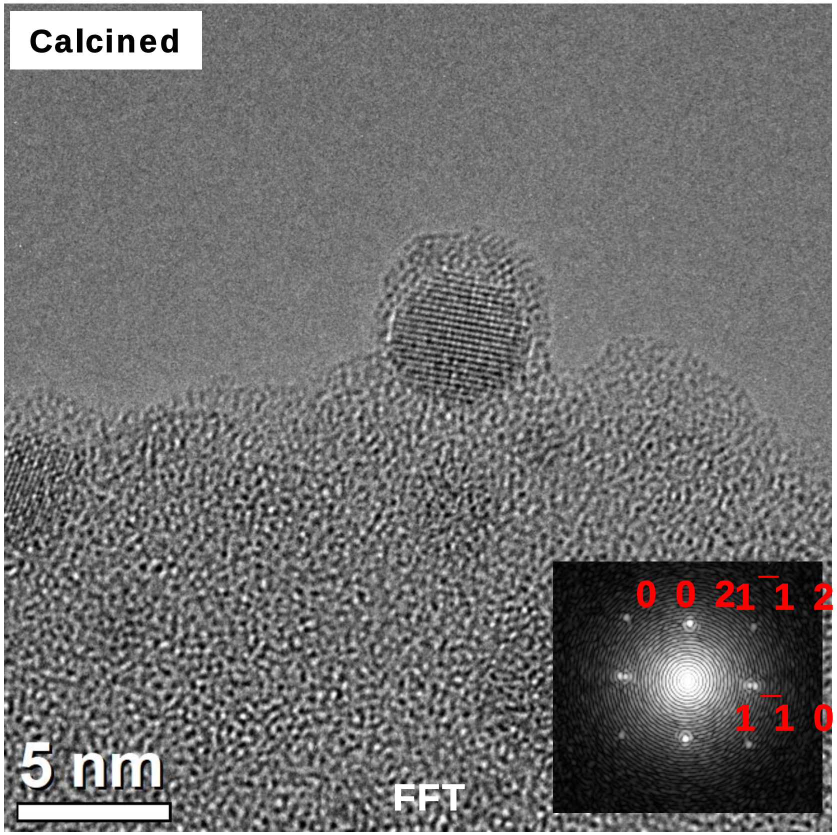
Pd_2Ga phase formed

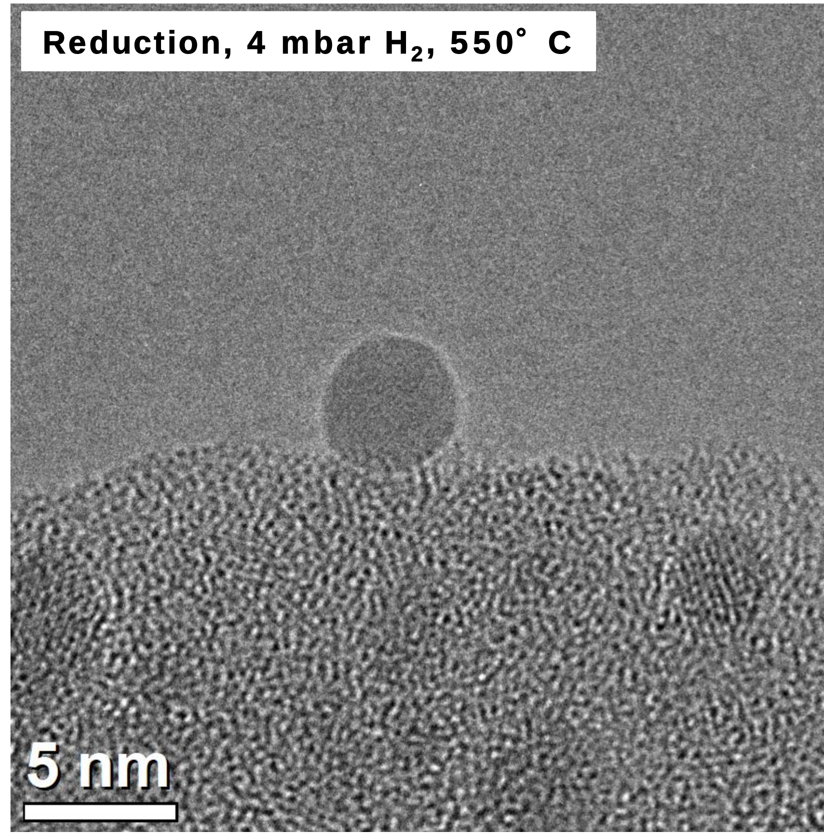
Ga fully reduced

Alloying mechanism (25 % H_2 in Ar) – one explanation



Alloying mechanism – preliminary data





Pressure gap